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(54) **Process for the modification of a material surface**

(57) The invention relates to a process for coating a material surface, comprising the steps of:

- (a) covalently binding polymerization initiator radicals to the surface;
- (b) grafts polymerizing a vinyl monomer carrying a reactive group onto the initiator-modified material surface and thereby providing a primary polymer coating comprising reactive groups; and
- (c) reacting the reactive groups of the primary polymer coating with a hydrophilic telomer having a functional group that is coreactive with the reactive groups of the primary polymer coating.

The coated articles that are obtainable by the process of the invention have desirable characteristics regarding adherence to the substrate, durability, hydrophilicity, wettability, biocompatibility and permeability and are thus useful for the manufacture of biomedical articles such as ophthalmic devices.

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Description

[0001] The present invention relates to a process for the manufacture of coated articles wherein the coating comprises a polymer having desirable characteristics regarding adherence to the substrate, durability, hydrophilicity, wettability, biocompatibility and permeability. More particular, the present invention relates to a process for the modification of the surface of an article, such as a biomedical material or article, especially a contact lens including an extended-wear contact lens wherein the articles are at least partly coated with a polymer having a "bottle-brush" type structure composed of tethered "hairy" chains.

[0002] A variety of different types of processes for preparing polymeric coatings on a substrate have been disclosed in the prior art. For example, U.S. patent No. 5,527,925 describes functionalized photoinitiators and also organic substrates such as contact lenses containing said photoinitiators covalently bound to their surface. In one embodiment of said disclosure, the so modified surface of the contact lens is further coated with a photopolymerizable ethylenically unsaturated monomer which is then polymerized by irradiation thus forming a novel substrate surface. With this method, however, it is not always possible to obtain the desired coating characteristics, for example wettability characteristics which are necessary for the surface of biomedical devices including contact lenses. In particular, the ability of the known materials to attract and stabilize a continuous layer of an aqueous solution, e.g. human body fluids such as tears or mucus layers, for a prolonged period of time which is an important feature for many biomedical applications is not yet satisfactory.

[0003] Surprisingly, it now has been found that articles, particularly biomedical devices such as contact lenses, with an improved wettability, water-retention ability and biocompatibility are obtained by first of all providing the article surface with covalently bound photoinitiator molecules, then grafting specific ethylenically unsaturated monomers comprising a reactive group onto the material surface, and finally reacting the reactive groups of the tethered polymer chains that have been generated on the material surface with a hydrophilic moiety having a functional group that is coreactive with the reactive groups of the polymer chains.

[0004] The present invention therefore in one aspect relates to a process for coating a material surface, comprising the steps of:

- (a) covalently binding polymerization initiator radicals to the surface;
- (b) graft polymerizing a vinyl monomer carrying a reactive group onto the initiator-modified material surface and thereby providing a primary polymer coating comprising reactive groups; and
- (c) reacting the reactive groups of the primary polymer coating with a hydrophilic telomer having a functional group that is coreactive with the reactive groups of the primary polymer coating.

[0005] Examples of materials that may be coated according to the process of the invention are quartz, ceramics, glasses, silicate minerals, silica gels, metals, metal oxides, carbon materials such as graphite or glassy carbon, natural or synthetic organic polymers, or laminates, composites or blends of said materials, in particular natural or synthetic organic polymers which are known in large number. Some examples of polymers are polyaddition and polycondensation polymers (polyurethanes, epoxy resins, polyethers, polyesters, polyamides and polyimides); vinyl polymers (polyacrylates, polymethacrylates, polystyrene, polyethylene and halogenated derivatives thereof, polyvinyl acetate and polyacrylonitrile); elastomers (silicones, polybutadiene and polyisoprene); or modified or unmodified biopolymers (collagen, cellulose, chitosan and the like).

[0006] A preferred group of materials to be coated are those being conventionally used for the manufacture of biomedical devices, e.g. contact lenses, in particular contact lenses for extended wear, which are not hydrophilic per se. Such materials are known to the skilled artisan and may comprise for example polysiloxanes, perfluoropolyethers, fluorinated poly(meth)acrylates or equivalent fluorinated polymers derived e.g. from other polymerizable carboxylic acids, polyalkyl (meth)acrylates or equivalent alkylester polymers derived from other polymerizable carboxylic acids, or fluorinated polyolefines, such as fluorinated ethylene propylene, or tetrafluoroethylene, preferably in combination with specific dioxols, such as perfluoro-2,2-dimethyl-1,3-dioxol. Examples of suitable bulk materials are e.g. Lotafilcon A, Neofacon, Pasifacon, Telefocon, Silafocon, Fluorsilfocon, Paflufocon, Silafocon, Elastofilcon, Fluorofacon or Teflon AF materials, such as Teflon AF 1600 or Teflon AF 2400 which are copolymers of about 63 to 73 mol % of perfluoro-2,2-dimethyl-1,3-dioxol and about 37 to 27 mol % of tetrafluoroethylene, or of about 80 to 90 mol % of perfluoro-2,2-dimethyl-1,3-dioxol and about 20 to 10 mol % of tetrafluoroethylene.

[0007] Another preferred group of materials to be coated are those being conventionally used for the manufacture of biomedical devices, e.g. contact lenses, which are hydrophilic per se, since reactive groups, e.g. carboxy, carbamoyl, sulfate, sulfonate, phosphate, amine, ammonium or hydroxy groups, are inherently present in the material and therefore also at the surface of a biomedical device manufactured therefrom. Such materials are known to the skilled artisan and comprise for example polyhydroxyethyl acrylate, polyhydroxyethyl methacrylate (HEMA), polyvinyl pyrrolidone (PVP), polyacrylic acid, polymethacrylic acid, polyacrylamide, polydimethylacrylamide (DMA), polyvinyl alcohol or copolymers

for example from two or more monomers from the group hydroxyethyl acrylate, hydroxyethyl methacrylate, N-vinyl pyrrolidone, acrylic acid, methacrylic acid, acrylamide, dimethyl acrylamide, vinyl alcohol and the like. Typical examples are e.g. Polymacon, Tefilcon, Methafilcon, Deltafilcon, Bufilcon, Phemfilcon, Ocufilcon, Focofilcon, Etafilcon, Hefilcon, Vifilcon, Tetrafilcon, Perfilcon, Droxifilcon, Dimefilcon, Isofilcon, Mafilcon, Nelfilcon or Atlafilcon.

5 [0008] Still another group of preferred materials to be coated are amphiphilic segmented copolymers comprising at least one hydrophobic segment and at least one hydrophilic segment which are linked through a bond or a bridge member. Examples are silicone hydrogels, for example those disclosed in PCT applications WO 96/31792 and WO 97/49740 which are herewith incorporated by reference.

[0009] The material to be coated may also be any blood-contacting material conventionally used for the manufacture of renal dialysis membranes, blood storage bags, pacemaker leads or vascular grafts. For example, the material to be modified on its surface may be a polyurethane, polydimethylsiloxane, polytetrafluoroethylene, polyvinylchloride, Dacron™ or a composite made therefrom.

10 [0010] Moreover, the material to be coated may also be an inorganic or metallic base material with or without suitable reactive groups, e.g. ceramic, quartz, or metals, such as silicon or gold, or other polymeric or non-polymeric substrates. E.g. for implantable biomedical applications, ceramics or carbohydrate containing materials such as polysaccharides are very useful. In addition, e.g. for biosensor purposes, dextran coated base materials are expected to reduce nonspecific binding effects if the structure of the coating is well controlled. Biosensors may require polysaccharides on gold, quartz, or other non-polymeric substrates.

[0011] The form of the material to be coated may vary within wide limits. Examples are particles, granules, capsules, fibres, tubes, films or membranes, preferably moldings of all kinds such as ophthalmic moldings, in particular contact lenses.

[0012] In the initial state, the material to be coated carries initiator moieties for radical polymerization covalently bound to its surface. According to a preferred embodiment of the invention, the initiator moieties are covalently bound to the surface of the material to be modified on its surface via reaction of a functional group of the material surface with a reactive group of the initiator molecule.

25 [0013] Suitable functional groups may be inherently (a priori) present at the surface of the material to be modified on its surface. If substrates contain too few or no reactive groups, the material surface can be modified by methods known per se, for example plasma chemical methods (see, for example, WO 94/06485), or conventional functionalization with groups such as -OH, -NH₂ or -CO₂H produced. Suitable functional groups may be selected from a wide variety of groups well known to the skilled artisan. Typical examples are e.g. hydroxy groups, amino groups, carboxy groups, carbonyl groups, aldehyde groups, sulfonic acid groups, sulfonyl chloride groups, isocyanato groups, carboxy anhydride groups, lactone groups, azlactone groups, epoxy groups and groups being replaceable by amino or hydroxy groups, such as halo groups, or mixtures thereof. Amino groups and hydroxy groups are preferred.

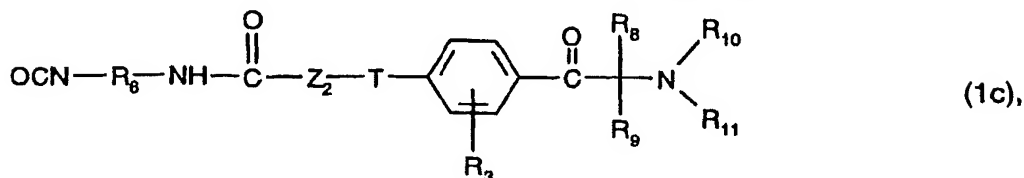
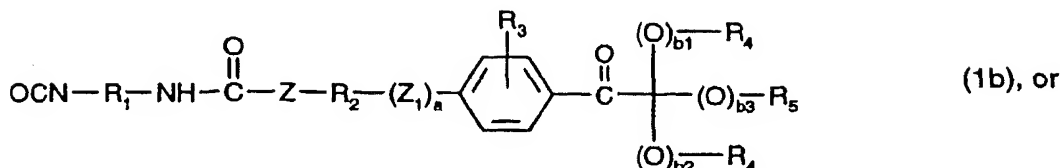
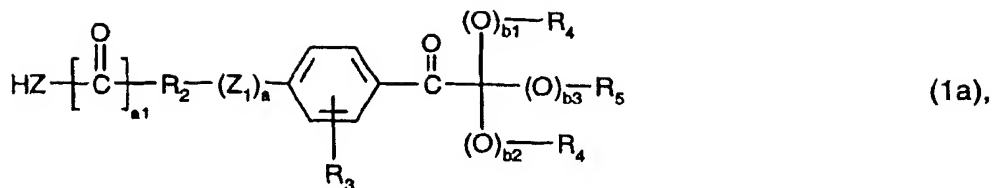
[0014] Polymerization initiators bound on the surface of the material to be coated are typically those that are initiating a radical polymerization of ethylenically unsaturated compounds. The radical polymerization may be induced thermally, or preferably by irradiation.

35 [0015] Suitable thermal polymerization initiators are known to the skilled artisan and comprise for example peroxides, hydroperoxides, azo-bis(alkyl- or cycloalkylnitriles), persulfates, percarbonates or mixtures thereof. Examples are benzoylperoxide, tert.-butyl peroxide, di-tert.-butyl-diperoxophthalate, tert.-butyl hydroperoxide, azo-bis(isobutyronitrile), 1,1'-azo-bis (1-cyclohexanecarbonitrile), 2,2'-azo-bis(2,4-dimethylvaleronitrile), 4,4'-azo-bis(4-cyano-valeric acid and the like. The thermal initiators may be linked to the surface of the bulk material by methods known per se, for example as disclosed in EP-A-0378511.

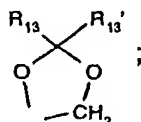
[0016] Initiators for the radiation-induced polymerization are particularly functional photoinitiators having a photoinitiator part and in addition a functional group that is coreactive with functional groups of the material surface, particularly with -OH, -NH₂, epoxy, carboxanhydride, alkylamino, -COOH or isocyanato groups. The photoinitiator part may belong to different types, for example to the thioxanthone type and preferably to the benzoin type. Suitable functional groups that are coreactive with the surface of the bulk material are for example a carboxy, hydroxy, epoxy or isocyanato group.

45 [0017] Preferred polymerization initiators for use in the present invention are the photoinitiators of formulae (I) and (Ia) as disclosed in US patent No. 5,527,925, those of the formula (I) as disclosed in PCT application WO 96/20919, or those of formulae II and III including formulae IIa-IIy and IIIg as disclosed in EP-A-0281941, particularly formulae IIb, III, IIIm, IIIn, IIp, IIr, IIs, IIx and IIIg therein. The respective portion of said three documents including the definitions and preferences given for the variables in said formulae are herewith included by reference.

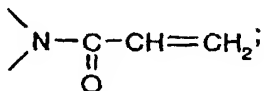
50 [0018] The polymerization initiator moieties are preferably derived from a functional photoinitiator of the formula



wherein Z is bivalent -O-, -NH- or -NR₁₂-; Z₁ is -O-, -O-(O)C-, -C(O)-O- or -O-C(O)-O-; R₃ is H, C₁-C₁₂-alkyl, C₁-C₁₂-alkoxy or N-C₁-C₁₂-alkylamino; R₄ and R₅ are each independently of the other H, linear or branched C₁-C₈-alkyl, C₁-C₈-hydroxyalkyl or C₆-C₁₀-aryl, or the groups R₄-(O)_{b1}- and R₄-(O)_{b2}- together are -(CH₂)_c- wherein c is an integer from 3 to 5, or the groups R₄-(O)_{b1}-, R₄-(O)_{b2}- and R₅-(O)_{b3}- together are a radical of the formula



R₂ is a direct bond or linear or branched C₁-C₈-alkylene that is unsubstituted or substituted by -OH and/or is interrupted or interrupted by one or more groups -O-, -O-C(O)- or -O-C(O)-O-; R₁ is branched C₃-C₁₈-alkylene, unsubstituted or C₁-C₄-alkyl- or C₁-C₄-alkoxy-substituted C₆-C₁₀-arylene, or unsubstituted or C₁-C₄-alkyl- or C₁-C₄-alkoxy-substituted C₇-C₁₈-aralkylene, unsubstituted or C₁-C₄-alkyl- or C₁-C₄-alkoxy-substituted C₃-C₈-cycloalkylene, unsubstituted or C₁-C₄-alkyl- or C₁-C₄-alkoxy-substituted C₃-C₈-cyclo-alkylene-C_yH_{2y}- or unsubstituted or C₁-C₄-alkyl- or C₁-C₄-alkoxy-substituted -C_yH_{2y}-(C₃-C₈-cycloalkylene)-C_yH_{2y}- wherein y is an integer from 1 to 6; R₆ independently has the same definitions as R₁ or is linear C₃-C₁₈-alkylene; R₁₂ is linear or branched C₁-C₆-alkyl; T is bivalent -O-, -NH-, -S-, C₁-C₈-alkylene or



Z₂ is a direct bond or -O-(CH₂)_d- wherein d is an integer from 1 to 6 and the terminal CH₂ group of which is linked to the adjacent T in formula (10c); R₈ is linear or branched C₁-C₈-alkyl, C₂-C₈-alkenyl or C₆-C₁₀-aryl-C₁-C₈-alkyl; R₉ independently of R₈ has the same definitions as R₈ or is C₆-C₁₀-aryl, or R₈ and R₉ together are -(CH₂)_e- wherein e is an integer from 2 to 6; R₁₀ and R₁₁ are each independently of the other linear or branched C₁-C₈-alkyl that may be substituted by C₁-C₄-alkoxy, or C₆-C₁₀-aryl-C₁-C₈-alkyl or C₂-C₈-alkenyl; or R₁₀ and R₁₁ together are -(CH₂)_{f1}-Z₃-(CH₂)_{f2}- wherein Z₃ is a direct bond, -O-, -S- or -NR₇-, and R₇ is H or C₁-C₈-alkyl and f₁ and f₂ are each independently of the other an integer from 2 to 4; R₁₃ and R₁₃' are each independently of the other H, C₁-C₈-alkyl, C₃-C₈-cycloalkyl, benzyl or phenyl; and a, a₁, b₁, b₂ and b₃ are each independently of the other 0 or 1; subject to the provisos that b₁ and b₂ are each 0 when R₁₅ is H; that the total of (b₁+b₂+b₃) is not exceeding 2; and that a is 0 when R₁₂ is a direct bond.

[0019] A preferred sub-group of compounds of formula (1a) or (1b) comprises those wherein, b₁ and b₂ are each

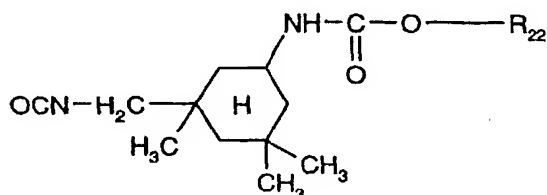
0; Z and Z₁ are each bivalent -O-; b₃ is 0 or 1; R₄ is C₁-C₄-alkyl or phenyl, or both groups R₄ together are tetramethylene or pentamethylene; R₅ is C₁-C₄-alkyl or H; R₃ is hydrogen; a and a₁ are each independently 0 or 1; R₂ is linear or branched C₂-C₄-alkylene, or is a direct bond, in which case a is 0; R₁ is branched C₅-C₁₀-alkylene, phenylene or phenylene substituted by from 1 to 3 methyl groups, benzylene or benzylene substituted by from 1 to 3 methyl groups, cyclohexylene or cyclohexylene substituted by from 1 to 3 methyl groups, cyclohexyl-C_yH_{2y}- or -C_yH_{2y}-cyclohexyl-C_yH_{2y}- or cyclohexyl-C_yH_{2y}- or -C_yH_{2y}-cyclohexyl-C_yH_{2y}- substituted by from 1 to 3 methyl groups; and y is 1 or 2.

[0020] An especially preferred sub-group of compounds of formula (1a) or (1b) comprises those wherein, b₁ and b₂ are each 0, Z and Z₁ are each bivalent -O-, b₃ is 0 or 1; R₄ is methyl or phenyl, or both groups R₄ together are pentamethylene; R₅ is methyl or H; R₃ is hydrogen; a is 1 and R₂ is ethylene, or a is 0 and R₂ is a direct bond; a₁ is 0 or 1; and R₁ is branched C₆-C₁₀-alkylene, phenylene or phenylene substituted by from 1 to 3 methyl groups, benzylene or benzylene substituted by from 1 to 3 methyl groups, cyclohexylene or cyclohexylene substituted by from 1 to 3 methyl groups, cyclohexyl-CH₂- or cyclohexyl-CH₂- substituted by from 1 to 3 methyl groups.

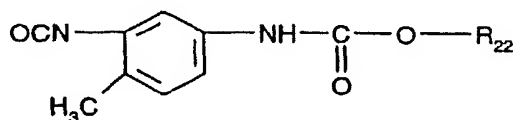
[0021] A preferred sub-group of compounds of formula (1c) comprises those wherein T is bivalent -O-, -NH-, -S- or -(CH₂)_y- wherein y is an integer from 1 to 6; Z₂ is a direct bond or -O-(CH₂)_y- wherein y is an integer from 1 to 6 and the terminal CH₂ group of which is linked to the adjacent T in formula (10c); R₃ is H, C₁-C₁₂-alkyl or C₁-C₁₂-alkoxy; R₈ is linear C₁-C₈-alkyl, C₂-C₈-alkenyl or C₆-C₁₀-aryl-C₁-C₈-alkyl; R₉ independently of R₈ has the same definitions as R₈ or is C₆-C₁₀-aryl, or R₈ and R₉ together are -(CH₂)_e- wherein e is an integer from 2 to 6; R₁₀ and R₁₁ are each independently of the other linear or branched C₁-C₈-alkyl that may be substituted by C₁-C₄-alkoxy, or C₆-C₁₀-aryl-C₁-C₈-alkyl or C₂-C₈-alkenyl; or R₁₀ and R₁₁ together are -(CH₂)_{f1}-Z₃-(CH₂)_{f2}- wherein Z₃ is a direct bond, -O-, -S- or -NR₇-, and R₇ is H or C₁-C₈-alkyl and f₁ and f₂ are each independently of the other an integer from 2 to 4; and R₆ is branched C₆-C₁₀-alkylene, phenylene or phenylene substituted by from 1 to 3 methyl groups, benzylene or benzylene substituted by from 1 to 3 methyl groups, cyclohexylene or cyclohexylene substituted by from 1 to 3 methyl groups, cyclohexylene-CH₂- or cyclohexylene-CH₂- substituted by from 1 to 3 methyl groups.

[0022] An especially preferred sub-group of compounds of formula (1c) comprises those wherein T is bivalent -O-; Z₂ is -O-(CH₂)_y- wherein y is an integer from 1 to 4 and the terminal CH₂ group of which is linked to the adjacent T in formula (10c); R₃ is H; R₈ is methyl, allyl, tolylmethyl or benzyl, R₉ is methyl, ethyl, benzyl or phenyl, or R₈ and R₉ together are pentamethylene, R₁₀ and R₁₁ are each independently of the other C₁-C₄-alkyl or R₁₀ and R₁₁ together are -CH₂CH₂OCH₂CH₂-, and R₆ is branched C₆-C₁₀-alkylene, phenylene or phenylene substituted by from 1 to 3 methyl groups, benzylene or benzylene substituted by from 1 to 3 methyl groups, cyclohexylene or cyclohexylene substituted by from 1 to 3 methyl groups, cyclohexylene-CH₂- or cyclohexylene-CH₂- substituted by from 1 to 3 methyl groups.

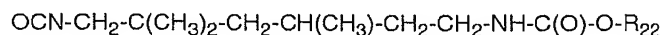
[0023] Some examples of especially preferred functional photoinitiators are the compounds of formulae



(11a),

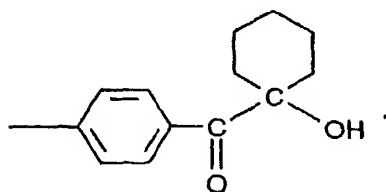
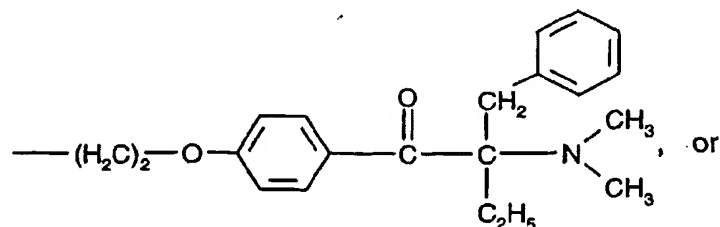
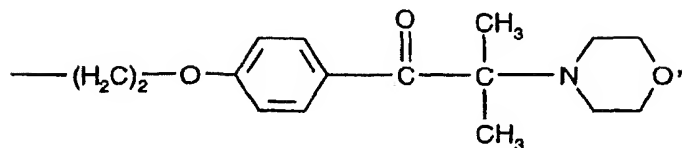
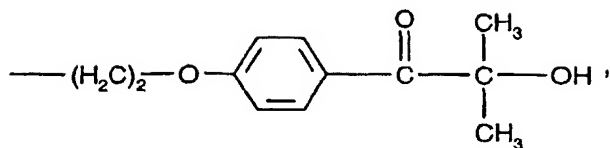


(11b),



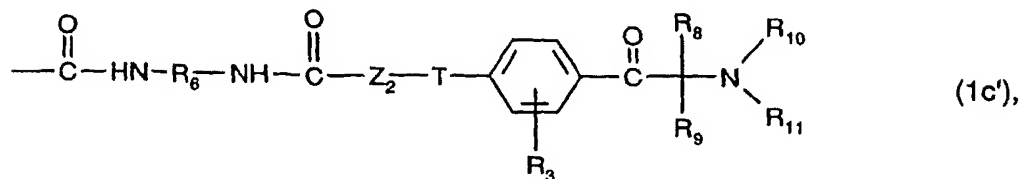
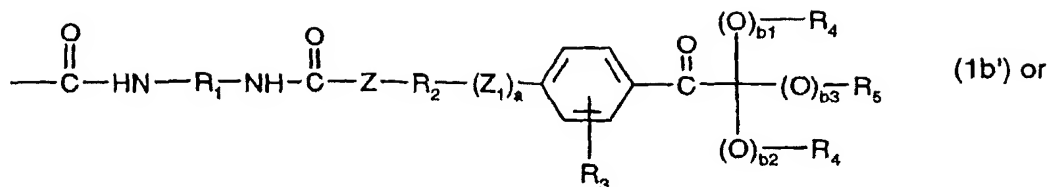
(11c),

wherein R₂₂ is a radical



[0024] In a preferred embodiment of the invention, the covalent binding between the inorganic or preferably material surface and the photoinitiator occurs via reaction of a hydroxy, amino, alkylamino, thiol or carboxy group, particularly of a hydroxy or amino group, of the substrate surface with an isocyanato group of the photoinitiator, for example using a photoinitiator of the above formula (1b), (1c), (11a), (11b) or (11c). Suitable methods for this are known, for example, from the above-mentioned documents. The reaction may be carried out, for example, at elevated temperature, for example from 0° to 100°C and preferably at room temperature, and optionally in the presence of a catalyst. After the reaction, excess compounds can be removed, for example, with solvents.

[0025] According to a preferred embodiment of the invention the material to be coated is an organic polymer containing H-active groups, in particular -OH, -NH₂ and/or -NH-, on the surface that are coreactive with isocyanato groups, in some or all of them an H-atom having been substituted by a radical of formula



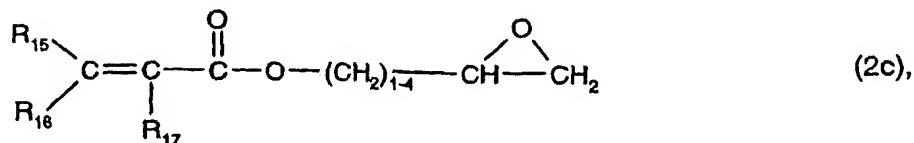
wherein for the variables R_1 - R_{11} , T, Z, Z_1 , Z_2 , a, b_1 , b_2 and b_3 the above-given meanings and preferences apply.

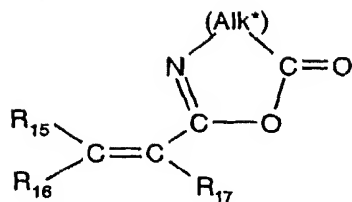
[0026] In another preferred embodiment of the invention, the covalent binding between the inorganic or preferably organic substrate and the photoinitiator occurs via reaction of a epoxy, carboxanhydride, lactone, azlactone or preferably isocyanato group of the substrate surface with a hydroxy, amino, alkylamino, thiol or carboxy group, particularly with a carboxy, hydroxy or amino group, of the photoinitiator, for example using a photoinitiator of the above formula (1a). This may be carried out, for example, by first reacting an above-mentioned bulk material containing H-active groups on the surface, in particular -OH, -NH₂ and/or -NH, selectively with one isocyanato group of a diisocyanate of formula OCN- R_1 -NCO, wherein R_1 has the above-given meanings, and then reacting the modified bulk material with a photoinitiator of the above-mentioned formula (1a).

[0027] Suitable reactive groups of the vinyl monomer according to step (b) are, for example, a hydroxy, amino, carboxy, carboxylic acid ester, carboxylic acid halide, carboxylic acid anhydride, epoxy, lactone, azlactone or isocyanato group. One group of preferred reactive groups comprises carboxy, carboxylic acid anhydride, azlactone or isocyanato, in particular isocyanato. Another group of preferred reactive groups comprises amino or in particular hydroxy.

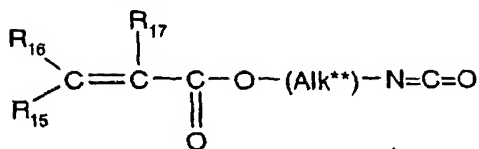
[0028] The vinyl monomer that is grafted onto the initiator-modified surface according to step (b) is, for example, an ethylenically unsaturated compound having from 2 to 18 C-atoms and preferably from 2 to 10 C-atoms which is substituted by a reactive group wherein the above-given meanings and preferences apply.

[0029] Suitable vinyl monomers having a reactive group are, for example, a compound of formula





(2d) or



(2e),

wherein R_{14} is hydrogen, unsubstituted or hydroxy-substituted C_1 - C_6 -alkyl or phenyl,
 R_{15} , and R_{16} are each independently of the other hydrogen, C_1 - C_4 -alkyl, phenyl, carboxy or halogen,
 R_{17} is hydrogen, C_1 - C_4 -alkyl or halogen,
 R_{18} and R_{18}' are each an ethylenically unsaturated radical having from 2 to 6 C-atoms, or
 R_{18} and R_{18}' together form a bivalent radical $-\text{C}(R_{15})=\text{C}(R_{17})-$ wherein R_{15} and R_{17} are as defined above, and
 (Alk^*) is C_1 - C_6 -alkylene, and (Alk^{**}) is C_2 - C_{12} -alkylene.

[0030] The following preferences apply to the variables contained in formulae (2a) - (2e):

R_{14} is preferably hydrogen or hydroxy- C_1 - C_4 -alkyl, in particular hydrogen or β -hydroxyethyl.

One of the variables R_{15} and R_{16} is preferably hydrogen and the other one is hydrogen, methyl or carboxy. Most preferably R_{15} and R_{16} are each hydrogen.

R_{17} is preferably hydrogen or methyl.

R_{18} and R_{18}' are preferably each vinyl or 1-methylvinyl, or R_{18} and R_{18}' together form a radical $-\text{C}(R_{15})=\text{C}(R_{17})-$ wherein R_{15} and R_{17} are each independently hydrogen or methyl.

(Alk^*) is preferably methylene, ethylene or 1,1-dimethyl-methylene, in particular a radical $-\text{CH}_2-$ or $-\text{C}(\text{CH}_3)_2-$.

(Alk^{**}) is preferably C_2 - C_4 -alkylene and in particular 1,2-ethylene.

[0031] Particularly preferred vinyl monomers having a reactive group are 2-isocyanatoethylmethacrylate (IEM), 2-vinyl-azlactone, 2-vinyl-4,4-dimethyl-azlactone, acrylic acid, methacrylic acid, acrylic acid anhydride, maleic acid anhydride, 2-hydroxyethylacrylate (HEA), 2-hydroxymethacrylate (HEMA), glycidylacrylate or glycidylmethacrylate.

[0032] Throughout the application terms such as carboxy, carboxylic acid, $-\text{COOH}$, sulfo, $-\text{SO}_3\text{H}$, amino, $-\text{NH}_2$ and the like always include the free acid or amine as well as a suitable salt thereof, for example a biomedically or in particular ocularly acceptable salt thereof such as, for example, a sodium, potassium, ammonium salt or the like (of an acid), or a hydrohalide such a hydrochloride (of an amine).

[0033] The vinyl monomer having a reactive group may be grafted as such or in admixture with a suitable vinyl comonomer, preferably a hydrophilic vinyl comonomer, onto the material surface.

[0034] The expression "hydrophilic vinyl comonomer" is understood to mean a monomer that typically produces as homopolymer a polymer that is water-soluble or capable of absorbing at least 10 % by weight water.

[0035] The proportion of vinyl comonomers, if used, is preferably from 0.1 to 10 units per vinyl monomer having a reactive group, especially from 0.25 to 5 units of vinyl comonomer per vinyl monomer having a reactive group and most preferably from 0.5 to 2 units per vinyl monomer having a reactive group.

[0036] Suitable hydrophilic vinyl comonomers include, without the following being an exhaustive list, C_1 - C_2 -alkyl acrylates and methacrylates, acrylamide, methacrylamide, N-mono- or N,N-di- C_1 - C_2 -alkylacrylamide and -methacrylamide, N-vinyl acetamide, N-acryloyl morpholine, ethoxylated acrylates and methacrylates, sodium ethylenesulfonate, sodium styrene-sulfonate, 2-acrylamido-2-methylpropanesulfonic acid, N-vinylpyrrole, N-vinylsuccinimide, five- to seven-membered N-vinyl lactams, 2- or 4-vinylpyridine, amino- (the term "amino" also including quaternary ammonium), mono- C_1 - C_2 -alkylamino- or di- C_1 - C_2 -alkylamino- C_1 - C_2 -alkyl acrylates and methacrylates, allyl alcohol and the like. Preferred are acrylamide, N,N-di- C_1 - C_2 -alkyl(meth)acrylamides such as N,N-dimethyl acrylamide or five- to seven-membered N-vinyl lactams such as N-vinylpyrrolidone.

[0037] Preferably, the vinyl monomer having a reactive group is grafted to the initiator-modified material surface in the absence of a vinyl comonomer.

[0038] The vinyl monomer having a reactive group, optionally in admixture with a vinyl comonomer, may be applied to the initiator-modified material surface and polymerized there according to processes known per se. For example, the material is immersed in a solution of the vinyl monomer(s), or a layer of vinyl monomer(s) is first of all deposited on the modified material surface, for example, by dipping, spraying, spreading, knife coating, pouring, rolling, spin coating or vacuum vapor deposition. Suitable solvents, if used in the polymerization process, are, for example, water, C₁-C₄-alcohols such as methanol or ethanol, glycols such as ethylene glycol or dipolar aprotic solvents such as, for example, acetonitrile, N,N-dimethyl formamide (DMF), N-methyl pyrrolidone (NMP), dimethyl sulfoxide (DMSO), N,N-dimethyl acetamide or acetone. The polymerization of the vinyl monomer(s) on the material surface then may be initiated, for example, thermally by the action of heat or preferably by irradiation, particularly by UV radiation. Suitable light sources for the irradiation are known to the artisan and comprise for example mercury lamps, high pressure mercury lamps, xenon lamps, carbon arc lamps or sunlight. The time period of irradiation may depend, for example, on the desired properties of the resulting composite material but is usually in the range of several seconds up to 30 minutes, preferably from 10 seconds to 10 minutes, and particularly preferably from 0.5 to 5 minutes. It can be advantageous to carry out the irradiation in an atmosphere of inert gas. After the polymerization, any non-covalently bound monomers, oligomers or polymers formed can be removed, for example by treatment with suitable solvents or by evaporation.

[0039] In case of a thermally initiated polymerization of the vinyl monomer(s) on the material surface said polymerization may be carried out, for example, at elevated temperature, for example at a temperature of from 35 to 100°C and preferably 40 to 80°C, for a time period of, for example, from 10 minutes to 48 hours and preferably 30 minutes to 36 hours in the absence or presence of one of the above-mentioned solvents. It can be advantageous to carry out the thermally initiated polymerization in an atmosphere of inert gas.

[0040] By means of the polymerization step (b), the vinyl monomer(s) may be grafted to the bulk material surface with formation of a primary coating comprising a plurality of polymer chains bound to the surface which form a so-called brush-type structure. Each polymer chain of said brush-type structure contains reactive groups at regular intervals (if the vinyl monomer comprising the reactive group is used without a vinyl comonomer) or statistically distributed (if the vinyl monomer comprising the reactive group is used in combination with a vinyl comonomer). The reactive groups that are present in the polymer chains are those mentioned before in the description of the vinyl monomers comprising a reactive group.

[0041] The hydrophilic telomer of step (c) is, for example, of formula



wherein X is a functional group that is coreactive with the reactive groups of the primary polymer coating obtainable according to step (b), for example hydroxy, epoxy, amino, C₁-C₆-alkylamino, carboxy or a suitable carboxy derivative thereof, for example a carboxylic acid ester or an acid halide, and (oligomer) denotes

(i) the radical of a telomer of formula



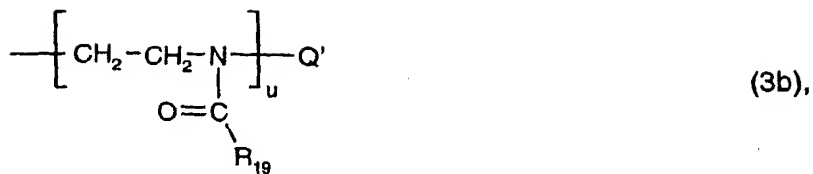
wherein (alk) is C₂-C₁₂-alkylene which may be interrupted by -O- or -NH-,

Q is a monovalent group that is suitable to act as a polymerization chain-reaction terminator,

p and q are each independently of another an integer from 0 to 350, wherein the total of (p+q) is an integer from 2 to 350,

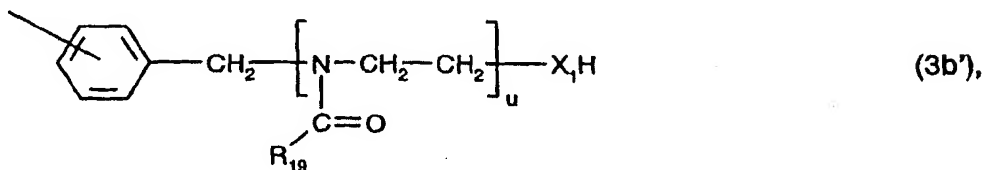
and B and B' are each independently of the other a 1,2-ethylene radical derivable from a copolymerizable vinyl monomer by replacing the vinylic double bond by a single bond, at least one of the radicals B and B' being substituted by a hydrophilic substituent; or

(ii) the radical of an oligomer of the formula



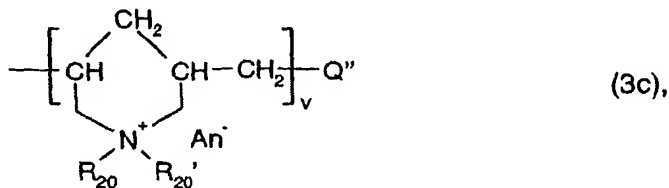
wherein R_{19} is hydrogen or unsubstituted or hydroxy-substituted C_1 - C_{12} -alkyl, u is an integer from 2 to 250 and Q' is a radical of a polymerization initiator; or

(iii) the radical of formula



wherein X_1 is $-\text{O}-$, $-\text{NH}-$ or $-\text{NC}_1\text{-C}_6\text{-alkyl-}$ and R_{19} and u are as defined above, or

(iv) the radical of an oligomer of formula



wherein R_{20} and R_{20}' are each independently C_1 - C_4 -alkyl, An^- is an anion, v is an integer from 2 to 250, and Q'' is a monovalent group that is suitable to act as a polymerization chain-reaction terminator; or

(v) the radical of an oligopeptide of formula

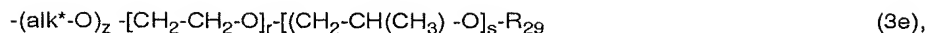


or



wherein R_{21} is hydrogen or C_1 - C_4 -alkyl which is unsubstituted or substituted by hydroxy, carboxy, carbamoyl, amino, phenyl, *o*-, *m*- or *p*-hydroxyphenyl, imidazolyl, indolyl or a radical $-\text{NH}-\text{C}(=\text{NH})-\text{NH}_2$ and t is an integer from 2 to 250, or the radical of an oligopeptide based on proline or hydroxyproline; or

(vi) the radical of a polyalkylene oxide of formula



wherein R_{29} is hydrogen or C_1 - C_{24} -alkyl, (alk^*) is C_2 - C_4 -alkylene, z is 0 or 1, r and s are each independently an integer from 0 to 250 and the total of $(r+s)$ is from 2 to 250; or

(vii) the radical of an oligosaccharide.

[0042] The following meanings and preferences apply to the variables contained in the definition of the hydrophilic telomer of formula (3):

X as carboxy derivative is for example a radical $-C(O)OC_1$ - C_4 -alkyl or $-C(O)Cl$. X is preferably hydroxy, amino or carboxy, more preferably amino or carboxy and in particular amino.

(alk) is preferably C_2 - C_8 -alkylene, more preferably C_2 - C_6 -alkylene, even more preferably C_2 - C_4 -alkylene and particularly preferably 1,2-ethylene. The alkylene radical (alk) may be branched or preferably linear alkylene.

Q is for example hydrogen.

[0043] The total of $(p+q)$ is preferably an integer from 2 to 150, more preferably from 5 to 100, even more preferably from 5 to 75 and particularly preferably from 5 to 50. In a preferred embodiment of the invention q is 0 and p is an integer from 2 to 350, preferably from 2 to 150, more preferably from 5 to 100, even more preferably from 5 to 75, and particularly preferably from 5 to 50.

[0044] Suitable hydrophilic substituents of the radicals B or B' may be non-ionic, anionic, cationic or zwitterionic substituents. Accordingly, the telomer chain of formula (3a) that contains monomer units B and/or B' may be a charged chain containing anionic, cationic and/or zwitterionic groups or may be an uncharged chain. In addition, the telomer chain may comprise a copolymeric mixture of uncharged and charged units. The distribution of the charges within the telomer, if present, may be random or blockwise.

[0045] In one preferred embodiment of the invention, the telomer radical of formula (3a) is composed solely of non-ionic monomer units B and/or B' . In another preferred embodiment of the invention, the telomer radical of formula (3a) is composed solely of ionic monomer units B and/or B' , for example solely of cationic monomer units or solely of anionic monomer units. Still another preferred embodiment of the invention is directed to telomer radicals of formula (3a) comprising nonionic units B and ionic units B' .

[0046] Suitable non-ionic substituents of B or B' include for example a radical C_1 - C_6 -alkyl which is substituted by one or more same or different substituents selected from the group consisting of $-OH$, C_1 - C_4 -alkoxy and $-NR_{23}R_{23}'$, wherein R_{23} and R_{23}' are each independently of another hydrogen or unsubstituted or hydroxy-substituted C_1 - C_6 -alkyl or phenyl; phenyl which is substituted by hydroxy, C_1 - C_4 -alkoxy or $-NR_{23}R_{23}'$, wherein R_{23} and R_{23}' are as defined above; a radical $-COOY$, wherein Y is C_1 - C_{24} -alkyl which is unsubstituted or substituted, for example, by hydroxy, C_1 - C_4 -alkoxy, $-O-Si(CH_3)_3$, $-NR_{23}R_{23}'$ wherein R_{23} and R_{23}' are as defined above, a radical $-O-(CH_2CH_2O)_{1-24}-E$ wherein E is hydrogen or C_1 - C_6 -alkyl, or a radical $-NH-C(O)-O-G$, wherein $-O-G$ is the radical of a saccharide with 1 to 8 sugar units or is a radical $-O-(CH_2CH_2O)_{1-24}-E$, wherein E is as defined above, or Y is C_5 - C_8 -cycloalkyl which is unsubstituted or substituted by C_1 - C_4 -alkyl or C_1 - C_4 -alkoxy, or is unsubstituted or C_1 - C_4 -alkyl- or C_1 - C_4 -alkoxy-substituted phenyl or C_7 - C_{12} -aralkyl; $-CONY_1Y_2$ wherein Y_1 and Y_2 are each independently hydrogen, C_1 - C_{12} -alkyl, which is unsubstituted or substituted for example by hydroxy, C_1 - C_4 -alkoxy or a radical $-O-(CH_2CH_2O)_{1-24}-E$ wherein E is as defined above, or Y_1 and Y_2 together with the adjacent N-atom form a five- or six-membered heterocyclic ring having no additional heteroatom or one additional oxygen or nitrogen atom; a radical $-OY_3$, wherein Y_3 is hydrogen; or C_1 - C_{12} -alkyl which is unsubstituted or substituted by $-NR_{23}R_{23}'$; or is a radical $-C(O)-C_1$ - C_4 -alkyl; and wherein R_{23} and R_{23}' are as defined above; or a five- to seven-membered heterocyclic radical having at least one N-atom and being bound in each case via said nitrogen atom.

[0047] Suitable anionic substituents of B or B' include for example C_1 - C_6 -alkyl which is substituted by $-SO_3H$, $-OSO_3H$, $-OPO_3H_2$ and $-COOH$; phenyl which is substituted by one or more same or different substituents selected from the group consisting of $-SO_3H$, $-COOH$, $-OH$ and $-CH_2-SO_3H$; $-COOH$; a radical $-COOY_4$, wherein Y_4 is C_1 - C_{24} -alkyl which is substituted for example by $-COOH$, $-SO_3H$, $-OSO_3H$, $-OPO_3H_2$ or by a radical $-NH-C(O)-O-G'$ wherein G' is the radical of an anionic carbohydrate; a radical $-CONY_5Y_6$ wherein Y_5 is C_1 - C_{24} -alkyl which is substituted by $-COOH$, $-SO_3H$, $-OSO_3H$, or $-OPO_3H_2$ and Y_6 independently has the meaning of Y_5 or is hydrogen or C_1 - C_{12} -alkyl; or $-SO_3H$; or a salt thereof, for example a sodium, potassium, ammonium or the like salt thereof.

[0048] Suitable cationic substituents of B or B' include C_1 - C_{12} -alkyl which is substituted by a radical $-NR_{23}R_{23}'R_{23}''An^+$, wherein R_{23} , R_{23}' and R_{23}'' are each independently of another hydrogen or unsubstituted or hydroxy-substituted C_1 - C_6 -alkyl or phenyl, and An^+ is an anion; or a radical $-C(O)OY_7$, wherein Y_7 is C_1 - C_{24} -alkyl which

is substituted by $-\text{NR}_{23}\text{R}_{23}'\text{R}_{23}''\text{An}^-$ and is further unsubstituted or substituted for example by hydroxy, wherein R_{23} , R_{23}' , R_{23}'' and An^- are as defined above.

[0049] Suitable zwitterionic substituents of B or B' include a radical $-\text{R}_{24}\text{-Zw}$, wherein R_{24} is a direct bond or a functional group, for example a carbonyl, carbonate, amide, ester, dicarboanhydride, dicarboimide, urea or urethane group; and Zw is an aliphatic moiety comprising one anionic and one cationic group each.

[0050] The following preferences apply to the hydrophilic substituents of B and B':

(i) non-ionic substituents: Preferred alkyl substituents of B or B' are $\text{C}_1\text{-C}_4$ -alkyl, in particular $\text{C}_1\text{-C}_2$ -alkyl, which is substituted by one or more substituents selected from the group consisting of $-\text{OH}$ and $-\text{NR}_{23}\text{R}_{23}'$, wherein R_{23} and R_{23}' are each independently of another hydrogen or $\text{C}_1\text{-C}_4$ -alkyl, preferably hydrogen, methyl or ethyl and particularly preferably hydrogen or methyl, for example $-\text{CH}_2\text{-NH}_2$, $-\text{CH}_2\text{-N}(\text{CH}_3)_2$.

Preferred phenyl substituents of B or B' are phenyl which is substituted by $-\text{NH}_2$ or $\text{N}(\text{C}_1\text{-C}_2\text{-alkyl})_2$, for example o-, m- or p-aminophenyl.

In case that the hydrophilic substituent of B or B' is a radical $-\text{COOY}$, Y as optionally substituted alkyl is preferably $\text{C}_1\text{-C}_{12}$ -alkyl, more preferably $\text{C}_1\text{-C}_6$ -alkyl, even more preferably $\text{C}_1\text{-C}_4$ -alkyl and particularly preferably $\text{C}_1\text{-C}_2$ -alkyl, each of which being unsubstituted or substituted as mentioned above. In case that the alkyl radical Y is substituted by $-\text{NR}_{23}\text{R}_{23}'$, the above-given meanings and preferences apply for R_{23} and R_{23}' .

Examples of suitable saccharide substituents $-\text{O-G}$ of the alkyl radical Y that is substituted by $-\text{NH-C(O)-O-G}$ are the radical of a mono- or disaccharide, for example glucose, acetyl glucose, methyl glucose, glucosamine, N-acetyl glucosamine, glucono lactone, mannose, galactose, galactosamine, N-acetyl galactosamine, fructose, maltose, lactose, fucose, saccharose or trehalose, the radical of an anhydrosaccharide such as levoglucosan, the radical of a glucosid such as octylglucosid, the radical of a sugar alcohol such as sorbitol, the radical of a sugar acid derivative such as lactobionic acid amide, or the radical of an oligosaccharide with a maximum of 8 sugar units, for example fragments of a cyclodextrin, starch, chitosan, maltotriose or maltohexaose. The radical $-\text{O-G}$ preferably denotes the radical of a mono- or disaccharide or the radical of a cyclodextrin fragment with a maximum of 8 sugar units. Particular preferred saccharide radicals $-\text{O-G}$ are the radical of trehalose or the radical of a cyclodextrin fragment. In case that the alkyl radical Y is substituted by a radical $-\text{O}-(\text{CH}_2\text{CH}_2\text{O})_{1-24}\text{-E}$ or $-\text{NH-C(O)-O-G}$ wherein $-\text{O-G}$ is $-\text{O}-(\text{CH}_2\text{CH}_2\text{O})_{1-24}\text{-E}$, the number of $(\text{CH}_2\text{CH}_2\text{O})$ units is preferably from 1 to 12 in each case and more preferably from 2 to 8. E is preferably hydrogen or $\text{C}_1\text{-C}_2$ -alkyl.

Y as $\text{C}_5\text{-C}_6$ -cycloalkyl is for example cyclopentyl or preferably cyclohexyl, each of which being unsubstituted or substituted for example by 1 to 3 $\text{C}_1\text{-C}_2$ -alkyl groups. Y as $\text{C}_7\text{-C}_{12}$ -aralkyl is for example benzyl.

Preferred nonionic radicals $-\text{COOY}$ are those wherein Y is $\text{C}_1\text{-C}_6$ -alkyl; or $\text{C}_2\text{-C}_6$ -alkyl which is substituted by one or two substituents selected from the group consisting of hydroxy; $-\text{C}_1\text{-C}_2$ -alkoxy; $-\text{O-Si}(\text{CH}_3)_3$; and $-\text{NR}_{23}\text{R}_{23}'$ wherein R_{23} and R_{23}' are each independently of another hydrogen or $\text{C}_1\text{-C}_4$ -alkyl; or Y is a radical $-\text{CH}_2\text{CH}_2\text{-O}-(\text{CH}_2\text{CH}_2\text{O})_{1-12}\text{-E}$ wherein E is hydrogen or $\text{C}_1\text{-C}_2$ -alkyl; or is a radical $-\text{C}_2\text{-C}_4$ -alkylene- NH-C(O)-O-G , wherein $-\text{O-G}$ is the radical of a saccharide.

More preferred non-ionic radicals $-\text{COOY}$ are those wherein Y is $\text{C}_1\text{-C}_4$ -alkyl; or $\text{C}_2\text{-C}_4$ -alkyl which is substituted by one or two substituents selected from the group consisting of $-\text{OH}$ and $-\text{NR}_{23}\text{R}_{23}'$ wherein R_{23} and R_{23}' are each independently of another hydrogen or $\text{C}_1\text{-C}_2$ -alkyl; or a radical $-\text{CH}_2\text{CH}_2\text{-O}-(\text{CH}_2\text{CH}_2\text{O})_{1-12}\text{-E}$ wherein E is hydrogen or $\text{C}_1\text{-C}_2$ -alkyl; or is a radical $-\text{C}_2\text{-C}_4$ -alkylene- NH-C(O)-O-G wherein $-\text{O-G}$ is the radical of a saccharide.

Particularly preferred radicals $-\text{COOY}$ comprise those wherein Y is $\text{C}_1\text{-C}_2$ -alkyl, particularly methyl; or $\text{C}_2\text{-C}_3$ -alkyl, which is unsubstituted or substituted by hydroxy or N,N-di- $\text{C}_1\text{-C}_2$ -alkylamino, or is a radical $-\text{C}_2\text{-C}_3$ -alkylene- NH-C(O)-O-G wherein $-\text{O-G}$ is the radical of trehalose or the radical of a cyclodextrin fragment with a maximum of 8 sugar units.

Preferred non-ionic substituents $-\text{C(O)-NY}_1\text{Y}_2$ of B or B' are those wherein Y_1 and Y_2 are each independently of the other hydrogen or $\text{C}_1\text{-C}_6$ -alkyl which is unsubstituted or substituted by hydroxy; or Y_1 and Y_2 together with the adjacent N-atom form a heterocyclic 6-membered ring having no further heteroatom or having one further N- or O-atom. Even more preferred meanings of Y_1 and Y_2 , independently of each other, are hydrogen or $\text{C}_1\text{-C}_4$ -alkyl which is unsubstituted or substituted by hydroxy; or Y_1 and Y_2 together with the adjacent N-atom form a N- $\text{C}_1\text{-C}_2$ -alkylpiperazino or morpholino ring. Particularly preferred non-ionic radicals $-\text{C(O)-NY}_1\text{Y}_2$ are those wherein Y_1 and Y_2 are each independently of the other hydrogen or $\text{C}_1\text{-C}_2$ -alkyl; or Y_1 and Y_2 together with the adjacent N-atom form a morpholino ring.

Preferred non-ionic substituents $-\text{OY}_3$ of B or B' are those wherein Y_3 is hydrogen, $\text{C}_1\text{-C}_4$ -alkyl which is unsubstituted or substituted by $-\text{NH}_2$ or $\text{N}(\text{C}_1\text{-C}_2\text{-alkyl})_2$, or is a group $-\text{C(O)C}_1\text{-C}_2\text{-alkyl}$. Y_3 is particularly preferred hydrogen or acetyl.

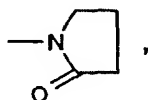
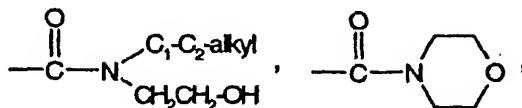
Preferred non-ionic heterocyclic substituents of B or B' are a 5- or 6-membered heteroaromatic or heteroaliphatic radical having one N-atom and in addition no further heteroatom or an additional N- or O- heteroatom, or is a 5 to 7-membered lactame. Examples of such heterocyclic radicals are N-pyrrolidonyl, 2- or 4-pyridinyl, 2-methyl

pyridin-5-yl, 2-, 3- oder 4-hydroxypyridinyl, N-ε-caprolactamyl, N-imidazolyl, 2-methylimidazol-1-yl, N-morpholinyl or 4-N-methylpiperazin-1-yl, particularly N-morpholinyl or N-pyrrolidonyl.

A group of preferred non-ionic substituents of B or B' comprises C₁-C₂-alkyl, which is unsubstituted or substituted by -OH or -NR₂₃R₂₃', wherein R₂₃ and R₂₃' are each independently of the other hydrogen or C₁-C₂-alkyl; a radical -COOY wherein Y is C₁-C₄-alkyl; C₂-C₄-alkyl which is substituted by -OH, -NR₂₃R₂₃' wherein R₂₃ and R₂₃' are each independently of another hydrogen or C₁-C₂-alkyl, or Y is a radical -C₂-C₄-alkylene-NH-C(O)-O-G wherein -O-G is the radical of a saccharide; a radical -C(O)-NY₁Y₂, wherein Y₁ and Y₂ are each independently of the other hydrogen or C₁-C₆-alkyl which is unsubstituted or substituted by hydroxy, or Y₁ and Y₂ together with the adjacent N-atom form a heterocyclic 6-membered ring having no further heteroatom or having one further N- or O-atom; a radical -OY₃, wherein Y₃ is hydrogen, C₁-C₄-alkyl which is unsubstituted or substituted by -NH₂ or -N(C₁-C₂-alkyl)₂, or is a group -C(O)C₁-C₂-alkyl; or a 5- or 6-membered heteroaromatic or heteroaliphatic radical having one N-atom and in addition no further heteroatom or an additional N-, O- or S-heteroatom, or a 5 to 7-membered lactame.

A group of more preferred non-ionic substituents of B or B' comprises a radical -COOY, wherein Y is C₁-C₂-alkyl, C₂-C₃-alkyl, which is substituted by hydroxy, amino or N,N-di-C₁-C₂-alkylamino, or is a radical -C₂-C₄-alkylene-NH-C(O)-O-G wherein -O-G is the radical of trehalose or a cyclodextrin fragment with a maximum of 8 sugar units; a radical -CO-NY₁Y₂, wherein Y₁ and Y₂ are each independently of the other hydrogen or C₁-C₄-alkyl which is unsubstituted or substituted by hydroxy, or Y₁ and Y₂ together with the adjacent N-atom form a N-C₁-C₂-alkylpiperazino or morpholino ring; or a heterocyclic radical selected from the group consisting of N-pyrrolidonyl, 2- or 4-pyridinyl, 2-methylpyridin-5-yl, 2-, 3- oder 4-hydroxypyridinyl, N-ε-caprolactamyl, N-imidazolyl, 2-methylimidazol-1-yl, N-morpholinyl and 4-N-methylpiperazin-1-yl.

A particularly preferred group of non-ionic substituents of B or B' comprises the radicals -CONH₂, -CON(CH₃)₂, -CONH-(CH₂)₂-OH,



-COO-(CH₂)₂-N(CH₃)₂, and -COO(CH₂)₂₋₄-NHC(O)-O-G wherein -O-G is the radical of trehalose.

(ii) anionic substituents:

Preferred anionic substituents of B or B' are C₁-C₄-alkyl, in particular C₁-C₂-alkyl, which is substituted by one or more substituents selected from the group consisting of -SO₃H and -OPO₃H₂, for example -CH₂-SO₃H; phenyl which is substituted by -SO₃H or sulfomethyl, for example o-, m- or p-sulfophenyl or o-, m- or p-sulfomethylphenyl; -COOH; a radical -COOY₄, wherein Y₄ is C₂-C₆-alkyl which is substituted by -COOH, -SO₃H, -OSO₃H, -OPO₃H₂, or by a radical -NH-C(O)-O-G' wherein G' is the radical of lactobionic acid, hyaluronic acid or sialic acid, in particular C₂-C₄-alkyl which is substituted by -SO₃H or -OSO₃H; a radical -CONY₅Y₆ wherein Y₅ is C₁-C₆-alkyl substituted by sulfo, in particular C₂-C₄-alkyl substituted by sulfo, and Y₆ is hydrogen, for example the radical -C(O)-NH-C(CH₃)₂-CH₂-SO₃H; or -SO₃H; or a suitable salt thereof. Particular preferred anionic substituents of B or B' are -COOH, -SO₃H, o-, m- or p-sulfophenyl, o-, m- or p-sulfomethylphenyl or a radical -CONY₅Y₆ wherein Y₅ is C₂-C₄-alkyl substituted by sulfo, and Y₆ is hydrogen.

(iii) cationic substituents:

Preferred cationic substituents of B or B' are C₁-C₄-alkyl, in particular C₁-C₂-alkyl, which is in each case substituted by -NR₂₃R₂₃'R₂₃'⁺⁺An⁻; or a radical -C(O)OY₇ wherein Y₇ is C₂-C₆-alkyl, in particular C₂-C₄-alkyl, which is in each case substituted by -NR₂₃R₂₃'R₂₃'⁺⁺An⁻ and is further unsubstituted or substituted by hydroxy. R₂₃, R₂₃' and R₂₃'' are each independently of another preferably hydrogen or C₁-C₄-alkyl, more preferably methyl or ethyl and particularly preferably methyl. Examples of suitable anions An⁻ are Hal⁻, wherein Hal is halogen, for example Br⁻, F⁻, J⁻ or

particularly Cl^- , furthermore HCO_3^- , CO_3^{2-} , H_2PO_3^- , HPO_3^{2-} , PO_3^{3-} , HSO_4^- , SO_4^{2-} or the radical of an organic acid such as OCOCH_3^\cdot and the like. A particularly preferred cationic substituent of B or B' is a radical $-\text{C}(\text{O})\text{OY}_7$ wherein Y_7 is C_2 - C_4 -alkyl, which is substituted by $-\text{N}(\text{C}_1\text{-C}_2\text{-alkyl})_3^+\text{An}^-$ and is further substituted by hydroxy, and An^- is an anion, for example the radical $-\text{C}(\text{O})\text{O-CH}_2\text{-CH}(\text{OH})\text{-CH}_2\text{-N}(\text{CH}_3)_3^+\text{An}^-$.

(iv) zwitterionic substituents $-\text{R}_{24}\text{-Zw}$:

R_{24} is preferably a carbonyl, ester or amide functional group and more preferably an ester group $-\text{C}(\text{O})\text{-O-}$.

Suitable anionic groups of the moiety Zw are for example $-\text{COO}^-$, $-\text{SO}_3^-$, $-\text{OSO}_3^-$, $-\text{OPO}_3\text{H}^-$ or bivalent $-\text{O-PO}_2^-$ or $-\text{O-PO}_2^-\text{-O-}$, preferably a group $-\text{COO}^-$ or $-\text{SO}_3^-$ or a bivalent group $-\text{O-PO}_2^-$, and in particular a group $-\text{SO}_3^-$.

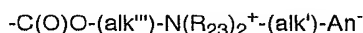
Suitable cationic groups of the moiety Zw are for example a group $-\text{NR}_{23}\text{R}_{23}'\text{R}_{23}''^+$ or a bivalent group $-\text{NR}_{23}\text{R}_{23}''^+$, wherein R_{23} , R_{23}' and R_{23}'' are as defined above, and are each independently of the other, preferably hydrogen or C_1 - C_6 -alkyl, preferably hydrogen or C_1 - C_4 -alkyl and most preferably each methyl or ethyl.

[0051] The moiety Zw is for example C_2 - C_{30} -alkyl, preferably C_2 - C_{12} -alkyl, and more preferably C_3 - C_8 -alkyl, which is in each case uninterrupted or interrupted by $-\text{O-}$ and substituted or interrupted by one of the above-mentioned anionic and cationic groups each, and, in addition, is further unsubstituted or substituted by a radical $-\text{OY}_8$, wherein Y_8 is hydrogen or the acyl radical of a carboxylic acid.

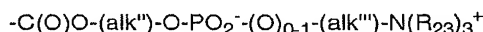
[0052] Y_8 is preferably hydrogen or the acyl radical of a higher fatty acid.

[0053] Zw is preferably C_2 - C_{12} -alkyl and even more preferably C_3 - C_8 -alkyl which is substituted or interrupted by one of the above-mentioned anionic and cationic groups each, and in addition may be further substituted by a radical $-\text{OY}_8$.

[0054] A preferred group of zwitter-ionic substituents $-\text{R}_{24}\text{-Z}$ corresponds to the formula

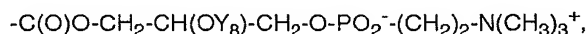


or



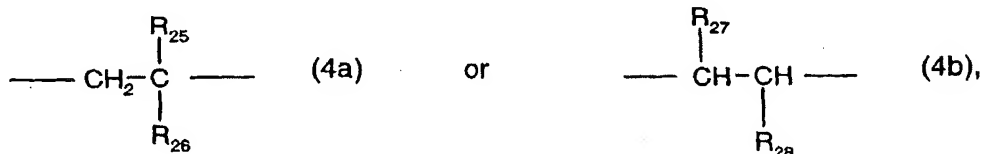
wherein R_{23} is hydrogen or C_1 - C_6 -alkyl; An^- is an anionic group $-\text{COO}^-$, $-\text{SO}_3^-$, $-\text{OSO}_3^-$ or $-\text{OPO}_3\text{H}^-$, preferably $-\text{COO}^-$ or $-\text{SO}_3^-$ and most preferably $-\text{SO}_3^-$, alk' is C_1 - C_{12} -alkylene, (alk'') is C_2 - C_{24} -alkylene which is unsubstituted or substituted by a radical $-\text{OY}_8$, Y_8 is hydrogen or the acyl radical of a carboxylic acid, and (alk''') is C_2 - C_8 -alkylene.

[0055] (alk') is preferably C_2 - C_8 -alkylene, more preferably C_2 - C_6 -alkylene and most preferably C_2 - C_4 -alkylene. (alk'') is preferably C_2 - C_{12} -alkylene, more preferably C_2 - C_6 -alkylene and particularly preferably C_2 - C_3 -alkylene which is in each case unsubstituted or substituted by hydroxy or by a radical $-\text{OY}_8$. (alk''') is preferably C_2 - C_4 -alkylene and more preferably C_2 - C_3 -alkylene. R_9 is hydrogen or C_1 - C_4 -alkyl, more preferably methyl or ethyl and particularly preferably methyl. A preferred zwitterionic substituent of B or B' is of formula



wherein Y_8 is hydrogen or the acyl radical of a higher fatty acid.

[0056] B denotes for example a radical of formula



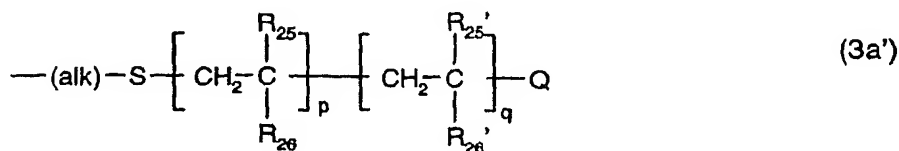
wherein R_{25} is hydrogen or C_1 - C_4 -alkyl, preferably hydrogen or methyl; R_{26} is a hydrophilic substituent, wherein the above given meanings and preferences apply; R_{27} is C_1 - C_4 -alkyl, phenyl or a radical $-\text{C}(\text{O})\text{OY}_9$, wherein Y_9 is hydrogen or unsubstituted or hydroxy-substituted C_1 - C_4 -alkyl; and R_{28} is a radical $-\text{C}(\text{O})\text{Y}_9'$ or $-\text{CH}_2\text{-C}(\text{O})\text{OY}_9'$ wherein Y_9' independently has the meaning of Y_9 .

[0057] R_{27} is preferably C_1 - C_2 -alkyl, phenyl or a group $-\text{C}(\text{O})\text{OY}_9$. R_{28} is preferably a group $-\text{C}(\text{O})\text{OY}_9'$ or $-\text{CH}_2\text{-C}(\text{O})\text{OY}_9'$ wherein Y_9 and Y_9' are each independently of the other hydrogen, C_1 - C_2 -alkyl or hydroxy- C_1 - C_2 -alkyl. Particularly preferred $-\text{CHR}_{27}\text{-CHR}_{28}-$ units according to the invention are those wherein R_{27} is methyl or a group $-\text{C}(\text{O})\text{OY}_9$ and R_{28} is a group $-\text{C}(\text{O})\text{OY}_9'$ or $-\text{CH}_2\text{-C}(\text{O})\text{OY}_9'$ wherein Y_9 and Y_9' are each hydrogen, C_1 - C_2 -alkyl or hydroxy- C_1 - C_2 -

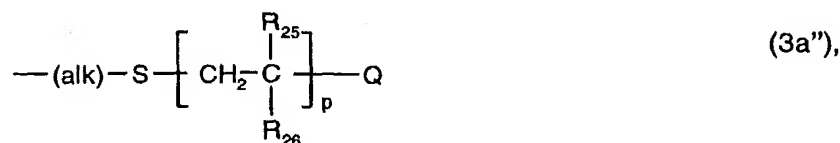
alkyl.

[0058] B' independently may have one of the meanings given above for B.

[0059] If (oligomer) is a telomer radical of formula (3a), the radical $-(\text{alk})-\text{S}-[\text{B}]_p-[\text{B}']_q-\text{Q}$ preferably denotes a radical of formula



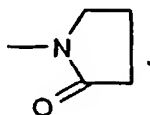
and even more preferably of the formula



wherein for R_{25} , R_{26} , Q, p and q the above-given meanings and preferences apply, for R_{25}' independently the meanings and preferences given before for R_{25} apply, and for R_{26}' independently the meanings and preferences given before for R_{26} apply.

[0060] A preferred group of suitable hydrophilic telomers according to the invention comprises compounds of the above formula (3) wherein for X the above given meanings and preferences apply, and (oligomer) is a radical of the above formula (3a'), wherein (alk) is C_2 - C_6 -alkylene, Q is a monovalent group that is suitable to act as a polymerization chain-reaction terminator, p and q are each an integer of from 0 to 100 and the total of (p+q) is from 5 to 100, R_{25} and R_{25}' are each independently of the other hydrogen or methyl, and for R_{26} and R_{26}' each independently of the other the meanings and preferences given before apply.

[0061] A particularly preferred group of suitable hydrophilic telomers according to the invention comprises compounds of the above formula (3) wherein X is amino or carboxy, and (oligomer) is a radical of the above formula (3a''), wherein (alk) is C_2 - C_4 -alkylene, Q is a monovalent group that is suitable to act as a polymerization chain-reaction terminator, p is an integer of from 5 to 100, R_{25} is hydrogen or methyl, and for R_{26} the above given meanings and preferences apply; in particular R_{26} of this embodiment is a radical $-\text{CONH}_2$, $-\text{CON}(\text{CH}_3)_2$ or



[0062] If (oligomer) is a radical (ii) of formula (3b), Q' in formula (3b) is for example C_1 - C_{12} -alkyl, phenyl or benzyl, preferably C_1 - C_2 -alkyl or benzyl and in particular methyl. R_{19} is preferably unsubstituted or hydroxy-substituted C_1 - C_4 -alkyl and in particular methyl. u is preferably an integer from 2 to 150, more preferably from 5 to 100, even more preferably from 5 to 75 and particularly preferably from 5 to 50.

[0063] If (oligomer) is a radical of formula (3b'), the above given meanings and preferences apply for the variables R_{19} and u contained therein. X_1 is preferably hydroxy or amino.

[0064] If (oligomer) denotes a radical (iv) of formula (3c), R_{20} and R_{20}' are each preferably ethyl or in particular methyl; v is preferably an integer from 2 to 150, more preferably from 5 to 100, even more preferably from 5 to 75 and particularly preferably from 5 to 50; Q'' is for example hydrogen; and An^- is as defined before.

[0065] If (oligomer) denotes an oligopeptide radical (v) of formula (3d) or (3d'), R_{21} is for example hydrogen, methyl, hydroxymethyl, carboxymethyl, 1-hydroxyethyl, 2-carboxyethyl, isopropyl, n-, sec. or iso-butyl, 4-amino-n-butyl, benzyl, p-hydroxybenzyl, imidazolylmethyl, indolylmethyl or a radical $-(\text{CH}_2)_3-\text{NH}-\text{C}(=\text{NH})-\text{NH}_2$. t is preferably an integer from 2 to 150, more preferably from 5 to 100, even more preferably from 5 to 75 and particularly preferably from 5 to 50.

[0066] If (oligomer) denotes a polyoxyalkylene radical (vi) of formula (3e), R_{29} is preferably hydrogen or C_1 - C_{18} -alkyl, more preferably hydrogen or C_1 - C_{12} -alkyl, even more preferably hydrogen, methyl or ethyl, and particularly pref-

erably hydrogen or methyl. (alk*) is preferably a C₂-C₃-alkylene radical. z is preferably 0. r and s are each independently preferably an integer from 0 to 100 wherein the total of (r+s) is 5 to 100. r and s are each independently more preferably an integer from 0 to 50 wherein the total of (r+s) is 8 to 50. In a particularly preferred embodiment of the polyoxyalkylene radicals (oligomer), r is an integer from 8 to 50 and particularly 9 to 25, and s is 0.

5 **[0067]** (oligomer) as the radical of an oligosaccharide (vii) may be, for example, a di- or polysaccharide including carbohydrate containing fragments from a biopolymer. Examples are the radical of a cyclodextrin, trehalose, cellobiose, maltotriose, maltohexaose, chitohexaose or a starch, hyaluronic acid, deacetylated hyaluronic acid, chitosan, agarose, chitin 50, amylose, glucan, heparin, xylan, pectin, galactan, glycosaminoglycan, mucin, dextran, aminated dextran, cellulose, hydroxyalkylcellulose or carboxyalkylcellulose oligomer, each of which with a molecular weight average weight
10 of, for example, up to 25000, preferably up to 10000. Preferably the oligosaccharide according to (vii) is the radical of a cyclodextrin with a maximum of 8 sugar units.

[0068] Formulae (3a), (3a') and (3e) are to be understood as a statistic description of the respective oligomeric radicals, that is to say, the orientation of the monomers and the sequence of the monomers (in case of copolymers) are not fixed in any way by said formulae. The arrangement of B and B' in formula (3a) or of the ethyleneoxide and propyleneoxide units in formula (3e) thus in each case may be random or blockwise.

[0069] The weight average molecular weight of the hydrophilic telomers according to step (c) depends principally on the desired properties and is for example from 300 to 25000, preferably from 300 to 12000, more preferably from 300 to 8000, even more preferably from 300 to 5000 and particularly preferably from 500 to 4000.

[0070] The compounds of the formula (3) are known compounds which are commercially available or may be prepared according to known methods. For example, the compounds of formula (3), wherein (oligomer) is a radical of formula (3a), may be prepared according to PCT application WO 92/09639 by copolymerizing one or more hydrophilic ethylenically unsaturated monomers in the presence of a functional chain transfer agent such as cysteamine hydrochloride, thioglycolic acid or the like.

[0071] The reactions of the reactive groups of the polymer coating obtained according to step (b) (= primary coating) with the hydrophilic telomer having co-reactive groups in step (c) are well-known in the art and may be carried out as described in textbooks of organic chemistry. For example, in case that the primary coating is derived from a vinyl monomer of formula (2e) or the like, the reaction of its isocyanato groups with a compound of formula (3) may be carried out in an inert organic solvent such as acetonitrile, an optionally halogenated hydrocarbon, for example petroleum ether, methylcyclohexane, toluene, chloroform, methylene chloride and the like, or an ether, for example diethyl ether, tetrahydrofuran, dioxane, or a more polar solvent such as DMSO, DMA, N-methylpyrrolidone, at a temperature of from 0 to 100°C, preferably from 0 to 50°C and particularly preferably at room temperature, optionally in the presence of a catalyst, for example a tertiary amine such as triethylamine or tri-n-butylamine, 1,4-diazabicyclooctane, or a tin compound such as dibutyltin dilaurate or tin dioctanoate. In addition, the reaction of the isocyanato groups of the primary coating with a compound of formula (3) wherein X is an amino group also may be carried out in an aqueous solution in the absence of a catalyst. It can be advantageous to carry out the above reactions under an inert atmosphere, for example under an nitrogen or argon atmosphere.

[0072] In case that the primary coating is derived from a vinyl monomer of formula (2d) or the like, the reaction of the azlactone groups with a compound of formula (3) wherein X is an amino or hydroxy group, may be carried out at room temperature or at elevated temperature, for example at about 20 to 75°C, in water, in a suitable organic solvent or mixtures thereof, for example in an aqueous medium or in an aprotic polar solvent such as DMF, DMSO, dioxane, acetonitrile and the like.

[0073] In case that the primary coating is derived from a vinyl monomer of formula (2c) or the like, the reaction of the epoxy groups with a compound of formula (3) wherein X is an amino group may be carried out, for example, at room temperature or at elevated temperature, for example at about 20 to 100°C, in water, in a suitable organic solvent or in mixtures thereof.

[0074] In case that the primary coating is derived from a vinyl monomer of formula (2c) or the like, the reaction of the epoxy groups with a compound of formula (3) wherein X is an hydroxy group may be carried out, for example, at room temperature or at elevated temperature, for example at about 20 to 100°C, in an aprotic medium using a base catalyst, for example Al(O-C₁-C₆-alkyl)₃ or Ti(O-C₁-C₆-alkyl)₃. The same applies to the reaction of a hydroxyalkyl substituted vinyl monomer of formula (2a) with a compound of formula (3) wherein X is an epoxy group.

[0075] In case that the primary coating is derived from a vinyl monomer of formula (2b) or the like, the reaction of the carboxylic acid anhydride with a compound of formula (3) wherein X is an amino or hydroxy group may be carried out as described in organic textbooks, for example in an aprotic solvent, for example one of the above-mentioned aprotic solvents, at a temperature from room temperature to about 100°C.

55 **[0076]** In case that the primary coating is derived from a vinyl monomer of formula (2a) or the like, the reaction of its carboxy groups with the hydroxy, amino or epoxy groups of a compound of formula (3), or the reaction of its amino or hydroxy groups with a compound of formula (3), wherein X is carboxy, may be carried out under the conditions that are customary for ester or amide formation, for example in an aprotic medium at a temperature from about room tem-

perature to about 100°C. In case of a carboxy containing compound of formula (2a) it is preferred to carry out the esterification or amidation reaction in the presence of an activating agent, for example N-ethyl-N'-(3-dimethylaminopropyl)carbodiimide (EDC), N-hydroxy succinimide (NHS) or N,N'-dicyclohexyl carbodiimide (DCC).

[0077] The coated material obtained according to the invention may be purified afterwards in a manner known per se, for example by washing or extraction with a suitable solvent such as water.

[0078] According to step (c) of the process of the invention, the brushes of the primary coating obtained according to step (b) are provided with side chains by reacting the reactive groups of the brushes with co-reactive hydrophilic telomers. Typically the final coating has a so-called bottle brush-type structure (BBT) composed of tethered "hairy" chains. The BBT structure of the coatings of the invention may be varied within wide limits, for example by a suitable choice of the vinylmonomer(s) and chain length in step (b), or by a suitable choice of the hydrophilic telomer in step (c). Such BBT structures in one embodiment comprise a long hydrophilic or hydrophobic backbone which carries relatively densely packed comparatively short hydrophilic side chains (called primary bottle brushes). Another embodiment relates to secondary bottle brushes which are characterized in that the hydrophilic side chains themselves carry densely packed hydrophilic "secondary" side chains. Polymeric coatings of said primary and secondary BBT structures to a certain extent mimic highly water-retaining structures occurring in the human body, for example in cartilage or mucosal tissue.

[0079] The coating thickness of the coated material surfaces obtained according to the process of the invention depends principally on the desired properties. It can be, for example, from 0.001 to 1000 µm, preferably from 0.005 to 100 µm, more preferably from 0.01 to 50 µm, even more preferably from 0.01 to 5 µm, especially preferably from 0.01 to 1 µm and particularly preferably from 0.01 to 0.5 µm.

[0080] A further embodiment of the invention relates to a material that is coated by the process of the invention.

[0081] The material that is coated by the process of the invention is, for example, an organic bulk material, preferably a biomedical device, e.g. an ophthalmic device, preferably a contact lens including both hard and particularly soft contact lenses, an intraocular lens or artificial cornea. Further examples are materials useful for example as wound healing dressings, eye bandages, materials for the sustained release of an active compound such as a drug delivery patch, moldings that can be used in surgery, such as heart valves, vascular grafts, catheters, artificial organs, encapsulated biologic implants, e.g. pancreatic islets, materials for prostheses such as bone substitutes, or moldings for diagnostics, membranes or biomedical instruments or apparatus.

[0082] The biomedical devices, e.g. ophthalmic devices obtained according to the invention have a variety of unexpected advantages over those of the prior art which make those devices very suitable for practical purposes, e.g. as contact lens for extended wear or intraocular lens. For example, they do have a high surface wettability which can be demonstrated by their contact angles, their water retention and their water-film break up time or pre-lens or on-eye tear film break up time (TBUT).

[0083] The TBUT plays an particularly important role in the field of ophthalmic devices such as contact lenses. Thus the facile movement of an eyelid over a contact lens has proven important for the comfort of the wearer; this sliding motion is facilitated by the presence of a continuous layer of tear fluid on the contact lens, a layer which lubricates the tissue/lens interface. However, clinical tests have shown that currently available contact lenses partially dry out between blinks, thus increasing friction between eyelid and the lens. The increased friction results in soreness of the eyes and reduced movement of the contact lenses. Now it has become feasible to considerably increase the TBUT of commercial contact lenses such as, for example, Focus Dailies™, Focus New Vues® or Lotrafilcon A lenses, by applying a surface coating according to the invention. On the base curve of a contact lens, the pronounced lubricity of the coating facilitates the on-eye lens movement which is essential for extended wear of contact lenses. Moreover, the materials obtained by the process of the invention provide additional effects being essential for lenses for extended wear, such as an increased thickness of the pre-lens tear film which contributes substantially to low microbial adhesion and resistance to deposit formation. Due to the extremely soft and lubricious character of the novel surface coatings, biomedical articles such as in particular contact lenses coated by the process of the invention show a superior wearing comfort including improvements with respect to late day dryness and long term (overnight) wear. The novel surface coatings moreover interact in a reversible manner with ocular mucus which contributes to the improved wearing comfort.

[0084] In addition, biomedical devices, e.g. ophthalmic devices such as contact lenses or corneal prostheses such as corneal inlays or onlays, coated by the process of the invention, have a very pronounced biocompatibility combined with good mechanical properties. For example, the devices are blood compatible and have a good tissue integration. In addition, there are generally no adverse eye effects observed, while the adsorption of proteins or lipids is low, also the salt deposit formation is lower than with conventional contact lenses. Generally, there is low fouling, low microbial adhesion and low bioerosion while good mechanical properties can be for example found in a low friction coefficient and low abrasion properties. Moreover, the dimensional stability of the materials obtained according to the invention is excellent. In addition, the attachment of a hydrophilic surface coating at a given bulk material according to the invention does not affect its visual transparency.

[0085] In summary, the ophthalmic devices obtained by the process of the invention, such as contact lenses, provide a combination of low spoilation with respect to cell debris, cosmetics, dust or dirt, solvent vapors or chemicals, with

a high comfort for the patient wearing such ophthalmic devices in view of the soft hydrogel surface which for example provides a very good on-eye movement of the ophthalmic device.

[0086] Biomedical devices such as renal dialysis membranes, blood storage bags, pacemaker leads or vascular grafts coated by the process of the invention resist fouling by proteins by virtue of the continuous layer of bound water, thus reducing the rate and extent of thrombosis. Blood-contacting devices fabricated according to the present invention are therefore haemocompatible and biocompatible.

[0087] In the examples, if not indicated otherwise, amounts are amounts by weight, temperatures are given in degrees Celsius. Tear break-up time values in general relate to the pre-lens tear film non-invasive break-up time (PLTF-NIBUT) that is determined following the procedure published by M. Guillon et al., Ophthalm. Physiol. Opt. 9, 355-359 (1989) or M. Guillon et al., Optometry and Vision Science 74, 273-279 (1997). Average advancing and receding water contact angles of coated and non-coated lenses are determined with the dynamic Wilhelmy method using a Krüss K-12 instrument (Krüss GmbH, Hamburg, Germany). Wetting force on the solid is measured as the solid is immersed in or withdrawn from a liquid of known surface tension.

Surface functionalization

Example A-1: 1,2-Diaminocyclohexane plasma coating (DACH)

[0088] Two dried Lotrafilcon A lenses (polysiloxane/perfluoroalkyl polyether copolymer) are, after extraction in isopropanol, toluene and again in isopropanol, placed on the glass holder within the plasma reactor equipped with an external ring electrode and a 27.13 MHz radiofrequency (RF) generator for the generation of an inductively-coupled, cold glow discharge plasma. The distance between the substrates and the lower edge of the plasma zone is 12 cm. The reactor is evacuated to a pressure of 0.008 mbar, and held at these conditions for one hour. Then, the argon plasma gas flow rate into the plasma zone of the reactor is set to 20 sccm (standard cubic centimeter), the pressure in the reactor is adjusted to 0.12 mbar and the RF generator is switched on. The plasma discharge of a power 250 Watts is maintained for a total period of 1 min (in order to clean and activate the lenses surfaces). Afterward the 1,2-DACH vapor is introduced into the reactor chamber from DACH reservoir (maintained at 24 °C) at 0.15 mbar for 1 min. After this, the following parameters for the plasma polymerization of DACH are chosen : Argon flow rate for plasma excitation = 5 sccm, Argon carrier gas flow rate for DACH transport = 5 sccm, temperature of the DACH evaporation unit = 24 °C, the distance between the lower edge of the plasma zone and the substrates = 5 cm, pressure = 0.2 mbar, and plasma power = 100 W. The lenses are treated for about 5 minutes with a pulsing glow discharge plasma (1 µsec. on, 3 µsec. off). After 5 minutes of deposition the plasma discharge is interrupted and DACH vapor is let to flow into reactor for other 5 min. The reactor is then evacuated and maintained for 30 minutes at a pressure 0.008 mbar in order to remove residual monomer and activated species. The internal pressure is brought to atmospheric by using dry nitrogen. The substrates are then turned over and the whole procedure is repeated to coat the other side of the substrates. The samples are then unloaded from the reactor and used for the subsequent photoinitiator linkage.

Example A-2: Surface binding of the reactive photoinitiator molecules

[0089] The aminofunctionalized contact lenses from Example A-1 are, immediately after plasma treatment with 1,2-DACH plasma, immersed into 1 % acetonitrile solution of the reactive photoinitiator (I) prepared by the addition reaction from isophorone diisocyanate and 4-(2-hydroxyethoxy)phenyl 2-hydroxy-2-propyl ketone (Darocure 2959) by the method described in EP 0 632 329. The amino groups on the lenses surfaces react with the isocyanato groups of the photoinitiator molecules for 12 hours. After this time, the lenses are withdrawn from the reaction solution, washed and extracted in acetonitrile for 8 hours and dried under reduced pressure for 2 hours. The dried lenses are subsequently used for photografting.

Example A-3: Surface binding of the reactive photoinitiator molecules

[0090] The aminofunctionalized contact lenses from Example A-1 are, immediately after plasma treatment with 1,2-DACH plasma, immersed into 1 % acetonitrile solution of the reactive photoinitiator (II) prepared by the addition reaction from isophorone diisocyanate and 2-ethyl-2-(dimethylamino)-1-[4-(2-hydroxyethoxy)phenyl]-4-penten-1-one by the method described in WO 96/20796. The amino groups on the lenses surfaces react with the isocyanato groups of the photoinitiator molecules for 16 hours. After this time, the lenses are withdrawn from the reaction solution, washed and extracted in acetonitrile for 12 hours and dried under reduced pressure for 2 hours. The dried lenses are subsequently used for photografting.

Photografting of reactive monomers**Example B-1:** Photografting of 2-isocyanatoethyl methacrylate (IEM) onto the contact lens surface

5 [0091] 1.0 g of IEM is dissolved in 9 ml of acetonitrile and the solution is stirred under argon flow for 5 minutes. Argon is then let to bubble through the solution for the period of about 10 minutes. The solution is then filtered through 0.45 μm Teflon filter and degassed with argon for additional 10 minutes. The filtered solution is then frozen in a flask in liquid nitrogen, the flask is evacuated under a high vacuum, transferred into a glove box and used for photografting. 1 ml of the IEM solution is introduced into a small Petri dish of a volume of about 3 ml in a glove box. The dried lens from

10 Example A-2, carrying covalently linked photoinitiator molecules on its surface, is then placed into this solution and an additional 1 ml of the degassed solution is added on the lens in order to cover the whole lens with the solution. After 5 minutes, the Petri dish with the lens in the solution is exposed to 15 mW ultraviolet light for a period of about 3 minutes. The lens is then turned over and the exposition is repeated by applying 15 mW UV light for an additional 3 minutes. The modified lens is then withdrawn from the solution, washed twice in dried acetonitrile, continuously extracted and

15 dried acetonitrile for 2 h.

[0092] **Example B-2:** Photografting of 2-vinyl-4,4-dimethyl azlactone onto the contact lens surface 1.5 g of 2-vinyl-4,4-dimethyl azlactone (VAL) are dissolved in 13.5 ml of acetonitrile and the solution is stirred under argon flow for 5 minutes. Argon is then let to bubble through the solution for the period of about 10 minutes. The solution is then filtered through 0.45 μm Teflon filter and degassed with argon for additional 10 minutes. The filtered solution is then frozen in

20 a flask in liquid nitrogen, the flask is evacuated under a high vacuum, transferred into a glove box and used for photografting. 1 ml of the VAL solution is introduced into a small Petri dish of a volume of about 3 ml in a glove box. The dried lens from Example A-3, carrying covalently linked photoinitiator molecules on its surface, is then placed into this solution and an additional 1 ml of the degassed solution is added on the lens in order to cover the whole lens with the solution. After

25 5 minutes, the Petri dish with the lens in the solution is exposed to 15 mW ultraviolet light for a period of about 3 minutes. The lens is then turned over and the exposition was repeated by applying 15 mW UV light for an additional 3 minutes. The modified lens is then withdrawn from the solution, washed twice in dried acetonitrile and continuously extracted in dried acetonitrile for 2 h.

30 **Examples B-3 to B-5:** Photografting of other reactive molecules onto the contact lens surface

[0093] The following reactive monomers are photografted onto the lens surface obtained according to Example A-2 using the process described in Examples B-1 and B-2:

Example	(a) Monomer used
B-3	Glycidyl methacrylate
B-4	Acrylic acid
B-5	Acrylic acid anhydride

Telomer synthesis**Example C-1:** Acrylamide telomer

[0094] A 1000 mL three-necked round bottom flask is charged with a solution of 17.5 g (154 mmol) cysteamine hydrochloride in 150 deionized water. 1.1 g (4 mmol) α,α' -azodisobutyramidine dihydrochloride and a solution of 142 g

50 (2 mol) acrylamide in 450 mL deionized water are added. The pH of the solution is adjusted to pH 3 by addition of 1 molar hydrochloric acid. An intensive cooler and an internal thermometer are connected to the flask. The apparatus is evacuated to 100 mbar and filled with argon. This is repeated five times. The mixture is heated to 60°C for three hours and then cooled to room temperature. An analytical sample is freeze-dried and the monomer conversion was determined by $^1\text{H-NMR}$ spectroscopy. No resonances corresponding to C=C double bonds can be detected, indicating >98

55 % conversion of the monomer.

The pH of the remaining mixture is adjusted to 10.5 by addition of 1 molar sodium hydroxide solution and diluted to a total volume of 1200 mL. Salts and low molecular weight residues such as unreacted chain transfer agent are removed by reverse osmosis using a Millipore Proscale system equipped with a Millipore Helicon RO-4 Nanomax 50 membrane

operating at a pressure of 15 bar. The product is isolated from the obtained retentate by freeze-drying. Yield: 102 g of a white powder.

The concentration of amino groups is determined by functional group titration, result 0.22 mmol/g NH₂ corresponding to an average molecular weight of the telomer of 4500 g/mol. GPC-analysis indicate a monomodal molecular weight distribution and the absence of high molecular weight polymer.

Example C-2: Acryloyl morpholine telomer

[0095] A 100 mL three-necked round bottom flask is charged with a solution of 1.6 g (14.3 mmol) cysteamine hydrochloride in 45 mL of 0.1 molar aqueous acetic acid. 55 mg (0.2 mmol) α,α' -azodiisobutyramidine dihydrochloride and 14.1 g (100 mmol) acryloyl morpholine are added. An intensive cooler and an internal thermometer are connected to the flask. The apparatus is evacuated to 100 mbar and filled with argon. This is repeated five times. The mixture is heated to 60°C for four hours and then cooled to room temperature. An analytical sample is freeze-dried and the monomer conversion is determined by ¹H-NMR spectroscopy. No resonances corresponding to C=C double bonds can be detected, indicating >98 % conversion of the monomer.

The remaining mixture is freeze-dried, dissolved in methanol and the telomer is precipitated in 2 liters of diethyl ether and collected by filtration.

[0096] The telomer is redissolved in 50 mL water and the pH is adjusted to 10.5 by addition of 143 mL 0.1 molar sodium hydroxide solution and then diluted with water to a total volume of 500 mL. Salts and residual low molecular weight components are removed by ultrafiltration using a UFP-1-E-4A cartridge from A/G Technology Corporation, Needham, MA. The concentration of amino-groups is determined by functional group titration, result 0.54 mmol/g NH₂ corresponding to an average molecular weight of the telomer of 1850 g/mol.

Example C-3: Telomer from α,α' -mono-isocyanatoethyl methacrylate trehalose

[0097] A 100 mL three-necked round bottom flask is charged with a solution of 3.8 g (33.4 mmol) cysteamine hydrochloride in 45 mL of 0.1 molar aqueous acetic acid. 55 mg (0.2 mmol) α,α' -azodiisobutyramidine dihydrochloride and 53 g (106 mmol) mono-isocyanatoethyl methacrylate trehalose are added. An intensive cooler and an internal thermometer are connected to the flask. The apparatus is evacuated to 100 mbar and filled with argon. This is repeated five times. The mixture is heated overnight to 60°C and then cooled to room temperature. The product precipitates in 2 liters of acetone and is isolated by filtration, yielding a slightly yellow colored powder. No resonances corresponding to C=C double bonds can be detected by ¹H-NMR spectroscopy, indicating >98 % conversion of the monomer.

The product is dissolved in 200 mL water and the pH is adjusted to 10.5 by addition of 107 mL 0.1 molar sodium hydroxide solution and then diluted with water to a total volume of 500 mL. Salts and residual low molecular weight components are removed by ultrafiltration using a UFP-1-E-4A cartridge from A/G Technology Corporation, Needham, MA. The concentration of amino-groups is determined by functional group titration, result 0.12 mmol/g NH₂ corresponding to an average molecular weight of the telomer of 8300 g/mol and a degree of polymerization of 16.

Example C-4: Co-telomerization of hydroxyethyl acrylamide and N-acryloyl morpholine

[0098] A 1000 mL three-necked round bottom flask is charged with a solution of 28.4 g (250 mmol) cysteamine hydrochloride in 400 mL deionized water. 407 mg (1.5 mmol) α,α' -azodiisobutyramidine dihydrochloride and 70.6 g (500 mmol) acryloyl morpholine and 28.8 g (250 mmol) N-hydroxyethyl acrylamide are added. An intensive cooler and an internal thermometer are connected to the flask. The apparatus is evacuated to 100 mbar and filled with argon. This is repeated five times. The mixture is heated to 60°C for four hours and then cooled to room temperature. An analytical sample is freeze-dried and the monomer conversion is determined by ¹H-NMR spectroscopy. No resonances corresponding to C=C double bonds can be detected, indicating >98 % conversion of the monomer.

The remaining mixture is adjusted to pH = 10 by addition of 30% KOH solution. Salts and low molecular weight residues such as unreacted chain transfer agent are removed by reverse osmosis using a Millipore Proscale system equipped with a Millipore Helicon RO-4 Nanomax 50 membrane operating at a pressure of 15 bar. The product is isolated from the obtained retentate by freeze-drying.

The concentration of amino-groups is determined by functional group titration, result 0.95 mmol/g NH₂ corresponding to an average molecular weight of the co-telomer of 1050 g/mol. GPC-analysis indicates a monomodal molecular weight distribution and the absence of high molecular weight polymer.

Example C-5: Acrylamide telomer

[0099] A 1000 mL round bottom flask is charged with a solution of 71.1 g (1 mol) acrylamide, 4.93 g (18.2 mmol)

α,α' -azodiisobutyramidine dihydrochloride and 4.93 g (36.4 mmol) Cysteamine-hydrochloride in 400 mL of water. The clear and slightly yellowish solution is acidified with a few drops of Hydrochloric Acid to pH3. The stirred acidic solution is evacuated to 50 mbar and filled with argon. This is repeated three times. With a constant stream of Argon, this solution is poured into a 500 ml dropping funnel which was put onto a 'flow-through-reactor' consisting of a 1000mL three-necked round-bottom flask, reflux condenser, thermometer, magnetic stirrer and a 30 cm Liebig-condenser, which is filled with glass wool. The whole apparatus is constantly purged with Argon.

The dropping funnel is put onto the Liebig condenser, which is heated to 65°C. The flask is heated to 60°C. Slowly the solution is dropped through the Liebig-condenser into the stirred flask. This takes 2.5 hrs in which the temperature in the flask is kept between 58-65°C. After the completion of the addition, the solution is stirred for 2hrs at 60°C.

NaOH is added to the clear and slightly yellowish solution until pH10 is reached. The product is cleaned through reverse osmosis, using Millipore cartridge with a cut-off at 1000 Da and freeze-dried. A bright-white solid product is obtained. The concentration of amino groups is determined via functional group titration (0.34mEq/g) which corresponds well with the sulfur-value of the elemental analysis (0.33mEq/g). M_n 2000g/Mol.

Preparation of bottlebrush-type coatings

Example D-1: Coupling of an isocyanate functionalized primary surface with an aminoterminated telomer

[0100] The dried lens from Example B-1, carrying covalently linked poly-IEM chains with isocyanate groups on its surface, is placed into an aqueous solution prepared from 0.6 g of aminofunctionalized telomer from Example C-5 and 3 ml of deionized water. The isocyanate groups on the lens surface react with amino groups of the telomer at 25 °C for 12 hours. The modified lens is then withdrawn from the solution, washed twice in distilled water, continuously extracted in ultra pure water for 16 h and analyzed by ATR-FTIR and contact angle measurements.

Water/air contact angles on the modified lens are 27° adv., 19° rec., 8° hysteresis. In comparison, the contact angles of the non-modified lens are 101° adv., 64° rec., 37° hysteresis. ATR-FTIR confirm the bottlebrush-type structure of the coating.

Example D-2: Coupling reaction of an isocyanate functionalized primary surface with an aminoterminated co-telomer

[0101] The dried lens from Example B-1, carrying covalently linked poly-IEM chains with isocyanate groups on its surface, is modified in a manner corresponding to Example D-1, using the aminoterminated co-telomer of Example C-4. Water/air contact angles on the modified lens are 55° adv., 41° rec., 14° hysteresis. In comparison, the contact angles of the non-modified lens are 101° adv., 64° rec., 37° hysteresis.

Example D-3: Coupling reaction of a lactone functionalized primary surface with an aminoterminated telomer

[0102] The dried lens from Example B-2, carrying covalently linked poly-VAL chains with reactive lactone groups on its surface, is placed into an aqueous solution prepared from 0.6 g of aminofunctionalized telomer from Example C-5 and 3 ml of deionized water. The lactone groups on the lens surface react with the amino groups of the telomer at 25 °C for 12 hours. The modified lens is then withdrawn from the solution, washed twice in distilled water, continuously extracted in ultra pure water for 16 h and analyzed by ATR-FTIR and contact angle measurements.

Water/air contact angles on the modified lens are 21° adv., 13° rec., 8° hysteresis. In comparison, the contact angles of the non-modified lens are 101° adv., 64° rec., 37° hysteresis. ATR-FTIR measurements confirm a bottlebrush-type structure of the coating.

Examples D-4 to D-9: Coupling reactions of other functionalized primary surfaces with aminoterminated telomers

[0103] Additional coupling reactions are carried out in accordance with the procedure described in Example D-1 but using the following functionalized lenses and co/telomers:

Example	Functionalized lens from Example	Telomer from Example	Contact angles Adv./ Rec./ Hyst.
D-4	B-1	C-2	61 / 47 / 14
D-5	B-1	C-3	28 / 17 / 11

(continued)

Example	Functionalized lens from Example	Telomer from Example	Contact angles Adv./ Rec./ Hyst.
D-6	B-2	C-3	34 / 19 / 15
D-7	B-2	C-2	66 / 48 / 18
D-8	B-5	C-1	43 / 29 / 14
D-9	B-5	C-4	56 / 24 / 32

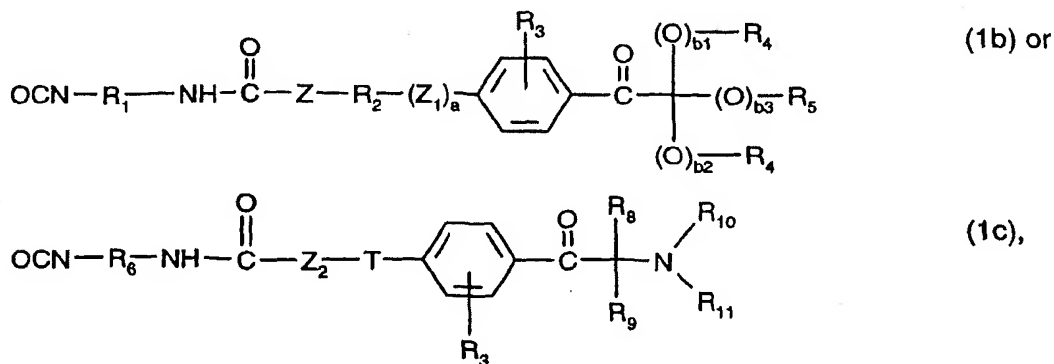
Claims

1. Process for coating a material surface, comprising the steps of:

- covalently binding polymerization initiator radicals to the material surface;
- graft polymerizing a vinyl monomer carrying a reactive group onto the initiator-modified material surface and thereby providing a primary polymer coating comprising reactive groups; and
- reacting the reactive groups of the primary polymer coating with a hydrophilic telomer having a functional group that is coreactive with the reactive groups of the primary polymer coating.

2. A process according to claim 1, wherein the material surface is the surface of a biomedical device comprising an organic bulk material.

3. A process according to claim 1 or 2, wherein in step (a) the surface already comprises or is provided with H-active groups that are coreactive with isocyanato groups, and said H-active groups are reacted with a polymerization initiator of formula

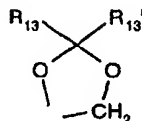


wherein R_1 is branched C_3 - C_{18} -alkylene, unsubstituted or C_1 - C_4 -alkyl- or C_1 - C_4 -alkoxy-substituted C_6 - C_{10} -arylene, or unsubstituted or C_1 - C_4 -alkyl- or C_1 - C_4 -alkoxy-substituted C_7 - C_{18} -aralkylene, unsubstituted or C_1 - C_4 -alkyl- or C_1 - C_4 -alkoxy-substituted C_3 - C_8 -cycloalkylene, unsubstituted or C_1 - C_4 -alkyl- or C_1 - C_4 -alkoxy-substituted C_3 - C_8 -cycloalkylene- C_yH_{2y} - or unsubstituted or C_1 - C_4 -alkyl- or C_1 - C_4 -alkoxy-substituted C_3 - C_8 -cycloalkylene- C_yH_{2y} - wherein y is an integer from 1 to 6;

R_2 is a direct bond or linear or branched C_1 - C_8 -alkylene that is unsubstituted or substituted by $-\text{OH}$ and/or is uninterrupted or interrupted by one or more groups $-\text{O}-$, $-\text{O}-\text{C}(\text{O})-$ or $-\text{O}-\text{C}(\text{O})-\text{O}-$;

R_3 is H, C_1 - C_{12} -alkyl, C_1 - C_{12} -alkoxy, N- C_1 - C_{12} -alkylamino or N,N-di- C_1 - C_{12} -alkylamino;

R_4 and R_5 are each independently of the other H, linear or branched C_1 - C_8 -alkyl, C_1 - C_8 -hydroxyalkyl or C_6 - C_{10} -aryl, or the groups $\text{R}_4-(\text{O})_{b_1}-$ and $\text{R}_4-(\text{O})_{b_2}-$ together are $-(\text{CH}_2)_c-$ wherein c is an integer from 3 to 5, or the groups $\text{R}_4-(\text{O})_{b_1}-$, $\text{R}_4-(\text{O})_{b_2}-$ and $\text{R}_5-(\text{O})_{b_3}-$ together are a radical of the formula



wherein R_{13} and

R_{13}' are each independently of the other H, C_1 - C_8 -alkyl, C_3 - C_8 -cycloalkyl, benzyl or phenyl;

Z is bivalent -O-, -NH- or -NR₁₂-, wherein R_{12} is linear or branched C_1 - C_6 -alkyl;

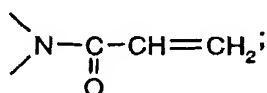
Z₁ is -O-, -O-(O)C-, -C(O)-O- or -O-C(O)-O-;

a, b₁, b₂ and b₃ are each independently of the other 0 or 1;

R_6 independently has the same definitions as R_1 or is linear C_3 - C_{18} -alkylene;

Z₂ is a direct bond or -O-(CH₂)_d- wherein d is an integer from 1 to 6 and the terminal CH₂ group of which is linked to the adjacent T in formula (10c);

T is bivalent -O-, -NH-, -S-, C_1 - C_8 -alkylene or



R_8 is linear or branched C_1 - C_8 -alkyl, C_2 - C_8 -alkenyl or C_6 - C_{10} -aryl- C_1 - C_8 -alkyl;

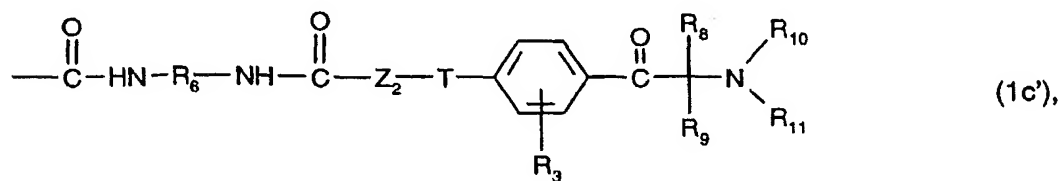
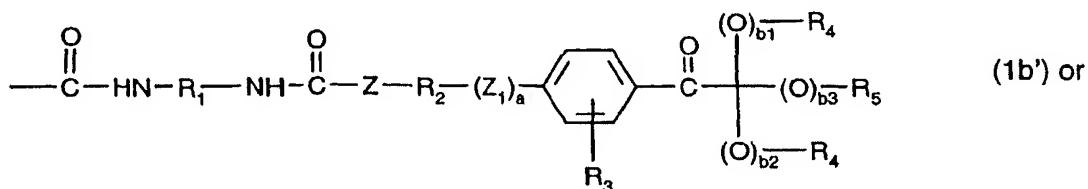
R_9 independently of R_8 has the same definitions as R_8 or is C_6 - C_{10} -aryl, or

R_8 and R_9 together are -(CH₂)_e- wherein e is an integer from 2 to 6;

R_{10} and R_{11} are each independently of the other linear or branched C_1 - C_8 -alkyl that may be substituted by C_1 - C_4 -alkoxy, or C_6 - C_{10} -aryl- C_1 - C_8 -alkyl or C_2 - C_8 -alkenyl; or R_{10} and R_{11} together are -(CH₂)_{f1}-Z₃-(CH₂)_{f2}- wherein Z₃ is a direct bond, -O-, -S- or -NR₇-, and R_7 is H or C_1 - C_8 -alkyl and f₁ and f₂ are each independently of the other an integer from 2 to 4;

subject to the provisos that b₁ and b₂ are each 0 when R_5 is H; that the total of (b₁+b₂+b₃) is not exceeding 2; and that a is 0 when R_2 is a direct bond.

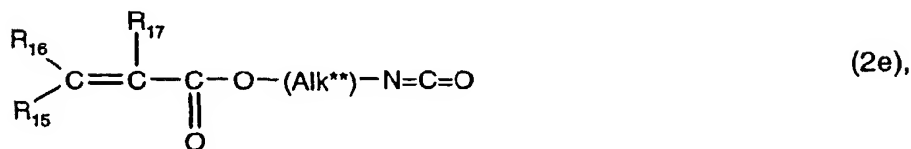
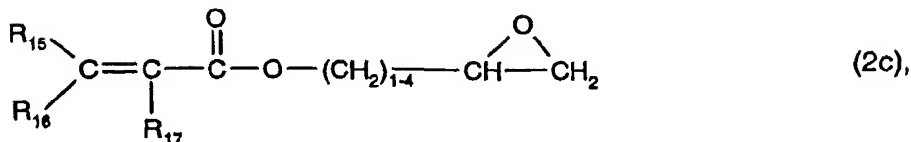
4. A process according to claim 3, wherein the surface is provided with H-active -OH, -NH₂ and/or -NH- groups, in some or all of them an H-atom having been substituted by a radical of formula



wherein the variables R_1 - R_{11} , T, Z, Z₁, Z₂, a, b₁, b₂ and b₃ are as defined in claim 3.

5. A process according to any one of claims 1 to 4, wherein the vinyl monomer according to step (b) is an ethylenically unsaturated compound having from 2 to 18 C-atoms which is substituted by a reactive group selected from the group consisting of a hydroxy, amino, carboxy, carboxylic acid halide, carboxylic acid ester, carboxylic acid anhydride, epoxy, lactone, azlactone and an isocyanato group.

6. A process according to any one of claims 1 to 5, wherein the vinyl monomer is of formula



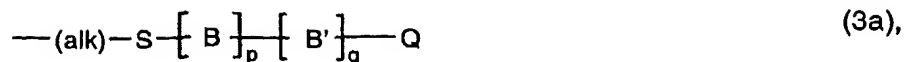
wherein R_{14} is hydrogen, unsubstituted or hydroxy-substituted C_1 - C_6 -alkyl or phenyl,
 R_{15} , and R_{16} each independently of the other is hydrogen, C_1 - C_4 -alkyl, phenyl, carboxy or halogen,
 R_{17} is hydrogen, C_1 - C_4 -alkyl or halogen,
 R_{18} and R_{18}' are each an ethylenically unsaturated radical having from 2 to 6 C-atoms, or
 R_{18} and R_{18}' together form a bivalent radical $-\text{C}(\text{R}_{15})=\text{C}(\text{R}_{17})-$ wherein R_{15} and R_{17} are as defined above, and
 (Alk^*) is C_1 - C_6 -alkylene, and (Alk^{**}) is C_2 - C_{12} -alkylene.

7. A process according to any one of claims 1 to 6, wherein the hydrophilic telomer of step (c) is of formula



wherein X is hydroxy, amino, C_1 - C_6 -alkylamino, carboxy or a carboxy derivative, and (oligomer) denotes

(i) the radical of a telomer of formula



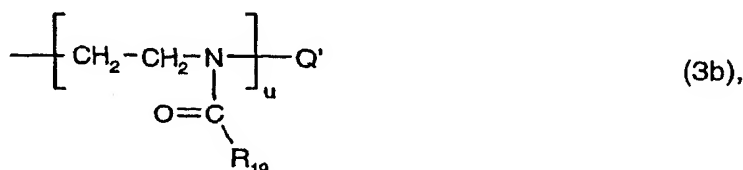
wherein (alk) is C₂-C₁₂-alkylene,

Q is a monovalent group that is suitable to act as a polymerization chain-reaction terminator,

p and q are each independently of another an integer from 0 to 350, wherein the total of (p+q) is an integer from 2 to 350,

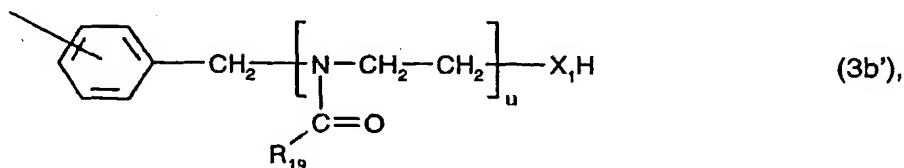
and B and B' are each independently of the other a 1,2-ethylene radical derivable from a copolymerizable vinyl monomer by replacing the vinylic double bond by a single bond, at least one of the radicals B and B' being substituted by a hydrophilic substituent; or

(ii) the radical of an oligomer of the formula

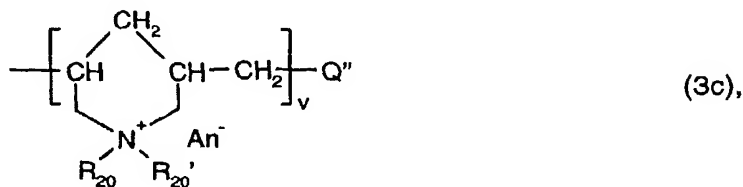


wherein R₁₉ is hydrogen or unsubstituted or hydroxy-substituted C₁-C₁₂-alkyl, u is an integer from 2 to 250 and Q' is a radical of a polymerization initiator; or

(iii) the radical of formula



wherein X₁ is -O-, -NH- or -NC₁-C₆-alkyl- and R₁₉, X and u are as defined above, or (iv) the radical of an oligomer of formula



wherein R₂₀ and R₂₀' are each independently C₁-C₄-alkyl, An⁻ is an anion, v is an integer from 2 to 250, and Q'' is a monovalent group that is suitable to act as a polymerization chain-reaction terminator;

(v) the radical of an oligopeptide of formula

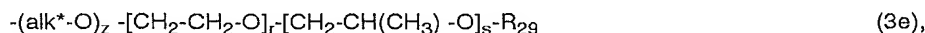


or



wherein R_{21} is hydrogen or C_1 - C_4 -alkyl which is unsubstituted or substituted by hydroxy, carboxy, carbamoyl, amino, phenyl, o-, m- or p-hydroxyphenyl, imidazolyl, indolyl or a radical $-NH-C(=NH)-NH_2$ and t is an Integer from 2 to 250, or the radical of an oligopeptide based on proline or hydroxyproline;

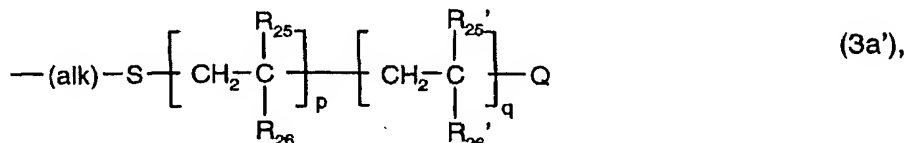
(vi) the radical of a polyalkylene oxide of formula



wherein R_{29} is hydrogen or C_1 - C_{24} -alkyl, (alk^*) is C_2 - C_4 -alkylene, z is 0 or 1, r and s are each independently an integer from 0 to 250 and the total of (r+s) is from 2 to 250; or

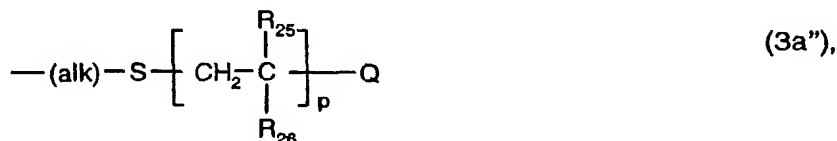
(vii) the radical of an oligosaccharide.

8. A process according to claim 7, wherein (oligomer) is a telomer radical of formula

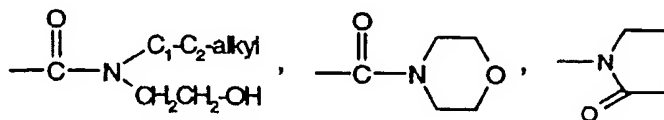


wherein (alk) is C_2 - C_6 -alkylene, Q is a monovalent group that is suitable to act as a polymerization chain-reaction terminator, p and q are each an integer of from 0 to 100 and the total of (p+q) is from 5 to 100, R_{25} and R_{25}' are each independently of the other hydrogen or methyl, and R_{26} and R_{26}' are each independently a radical $-COOY$, wherein Y is C_1 - C_2 -alkyl, C_2 - C_3 -alkyl, which is substituted by hydroxy, amino or N,N-di- C_1 - C_2 -alkylamino, or is a radical $-C_2$ - C_4 -alkylene- $NH-C(O)-O-G$ wherein $-O-G$ is the radical of trehalose or a cyclodextrin fragment with a maximum of 8 sugar units; or a radical $-CO-NY_1Y_2$, wherein Y_1 and Y_2 are each independently of the other hydrogen or C_1 - C_4 -alkyl which is unsubstituted or substituted by hydroxy, or Y_1 and Y_2 together with the adjacent N-atom form a N- C_1 - C_2 -alkylpiperazino or morpholino ring; or a heterocyclic radical selected from the group consisting of N-pyrrolidonyl, 2- or 4-pyridinyl, 2-methylpyridin-5-yl, 2-, 3- oder 4-hydroxypyridinyl, N-ε-caprolactamyl, N-imidazolyl, 2-methylimidazol-1-yl, N-morpholinyl and 4-N-methylpiperazin-1-yl.

9. A process according to claim 7, wherein (oligomer) is a telomer radical of formula



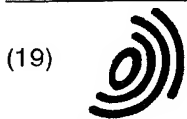
wherein (alk) is C_2 - C_4 -alkylene, Q is a monovalent group that is suitable to act as a polymerization chain-reaction terminator, p is an integer of from 5 to 100, R_{25} is hydrogen or methyl, and R_{26} is a radical $-CONH_2$, $-CON(CH_3)_2$, $-CONH-(CH_2)_2-OH$, $-COO-(CH_2)_2-N(CH_3)_2$,



or $-COO(CH_2)_{2,4}-NHC(O)-O-G$ wherein $-O-G$ is the radical of trehalose.

10. A coated material that is obtainable by the process of any one of claims 1 to 9.

11. A coated material according to claim 10, which is a biomedical device, preferably an ophthalmic device, in particular a contact lens, intraocular lens or artificial cornea.



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(54) **Process for the modification of a material surface**

(57) The invention relates to a process for coating a material surface, comprising the steps of:

- (a) covalently binding polymerization initiator radicals to the surface;
- (b) grafts polymerizing a vinyl monomer carrying a reactive group onto the initiator-modified material surface and thereby providing a primary polymer coating comprising reactive groups; and
- (c) reacting the reactive groups of the primary polymer coating with a hydrophilic telomer having a functional group that is coreactive with the reactive

groups of the primary polymer coating.

The coated articles that are obtainable by the process of the invention have desirable characteristics regarding adherence to the substrate, durability, hydrophilicity, wettability, biocompatibility and permeability and are thus useful for the manufacture of biomedical articles such as ophthalmic devices.

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European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	WO 96/20796 A (CIBA GEIGY AG ; CHABRECEK PETER (CH); LOHMANN DIETER (CH)) 11 July 1996 (1996-07-11) * the whole document *	1-11	C08J7/16 G02B1/04
A	US 4 914 004 A (KOEHLER MANFRED ET AL) 3 April 1990 (1990-04-03) * column 3, lines 18-26 *	1	
A,D	US 5 527 925 A (CHABRECEK PETER ET AL) 18 June 1996 (1996-06-18) * the whole document *	1-3	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			C08J G02B
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 22 March 2004	Examiner Meulemans, R
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